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(54) **GOLF BALL WITH SELECTED SPIN CHARACTERISTICS**

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CPC ***A63B 37/02*** (2013.01); ***A63B 37/0003*** (2013.01); ***A63B 37/0024*** (2013.01); ***A63B 37/0037*** (2013.01); ***A63B 37/0039*** (2013.01); ***A63B 37/0049*** (2013.01); ***A63B 37/0051*** (2013.01); ***A63B 37/0065*** (2013.01); ***A63B 37/0069*** (2013.01); ***A63B 37/0076*** (2013.01)

USPC **473/376**; 473/371; 473/373

(58) **Field of Classification Search**

None

See application file for complete search history.

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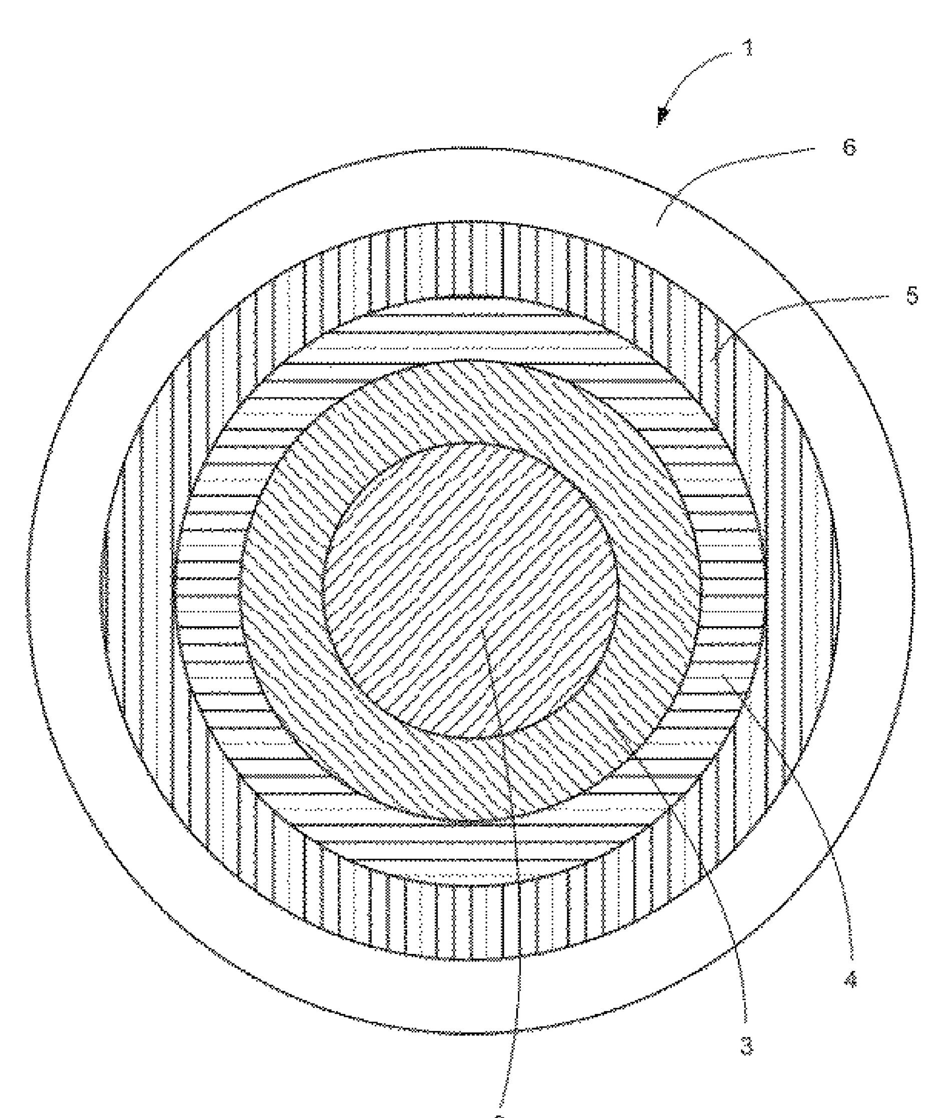
(57) **ABSTRACT**

A golf ball comprises (a) a core, (b) an inner mantle layer, (c) an intermediate mantle layer, (d) an outer mantle layer and (e) at least one cover layer, and the material flexural modulus (FM) of the core and the various layers follows the relationship FM(core)<FM(inner mantle)>FM(intermediate)<FM(outer mantle)>FM(cover), or the relationship FM(core)<FM(inner mantle)<FM(intermediate)>FM(outer mantle)>FM(cover).

48 Claims, 2 Drawing Sheets



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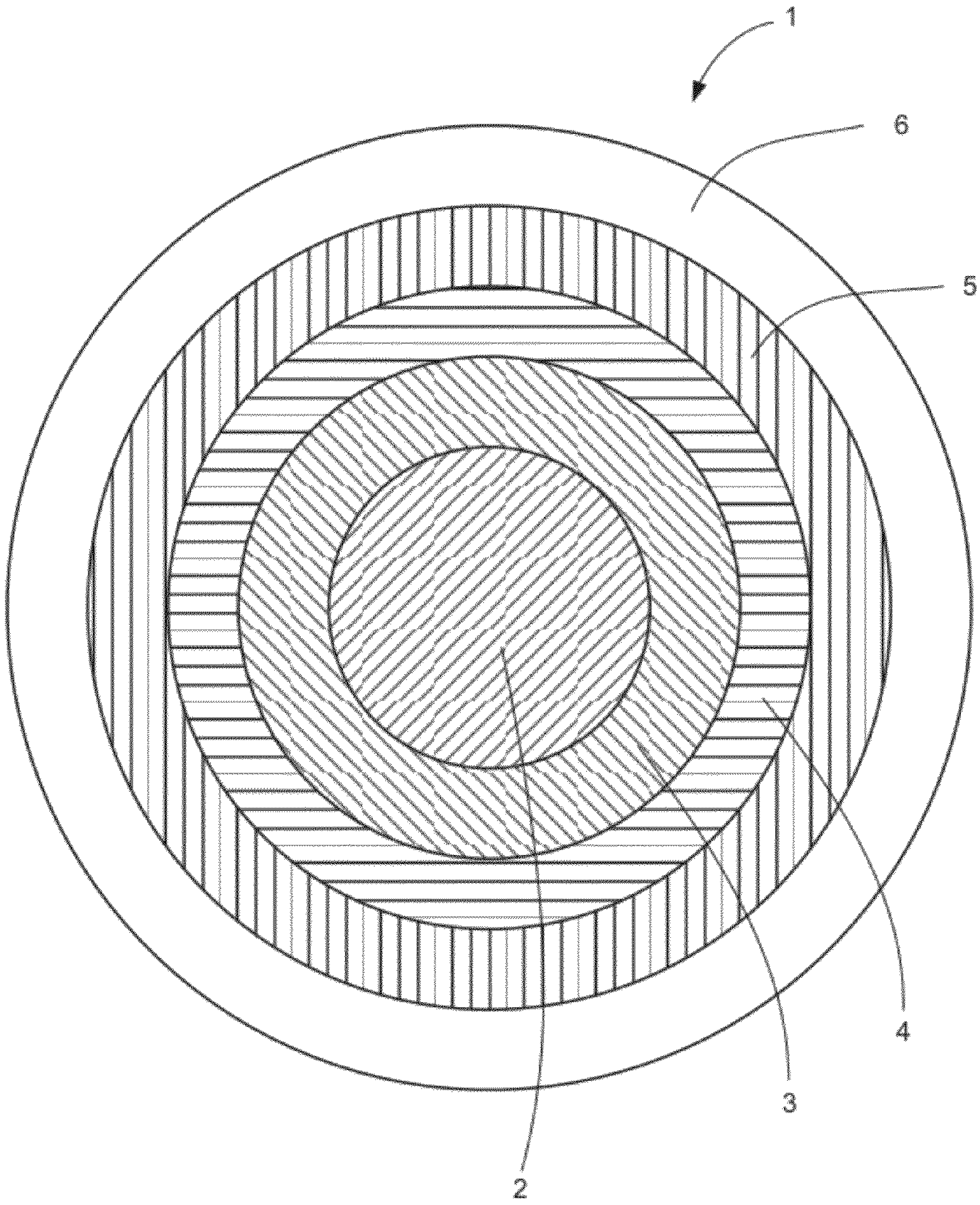

FIG. 1

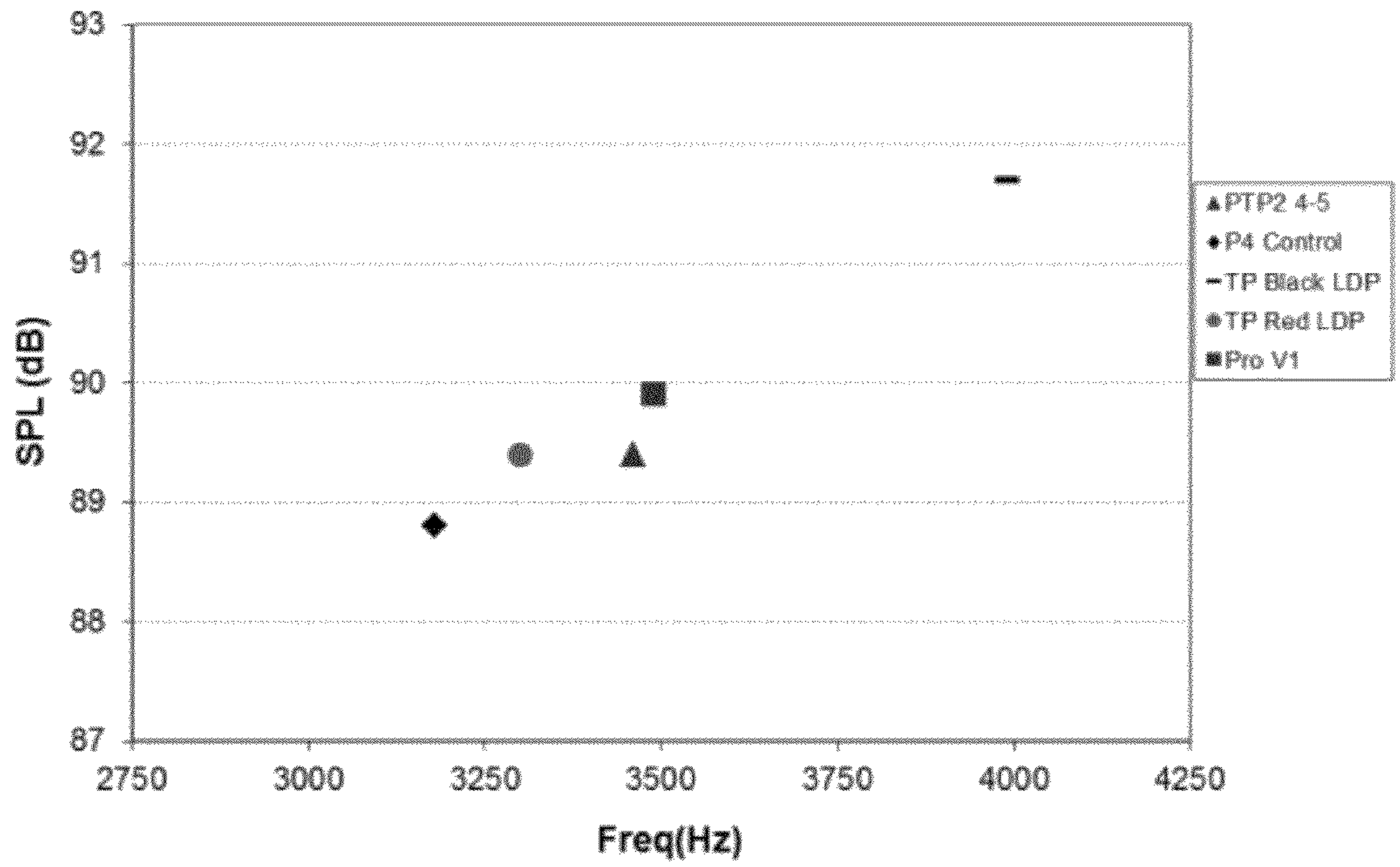
93
92
91
90
89
88
87
SPL (dB)
2750
3000
3250
3500
3750
4000
4250
Freq(Hz)
PTP2 4-5
P4 Control
TP Black LDP
TP Red LDP
Pro V1

FIG. 2

GOLF BALL WITH SELECTED SPIN CHARACTERISTICS

FIELD

This disclosure relates to golf balls.

BACKGROUND

"Multi-layer" golf balls generally include at least three "pieces," i.e., a central core and at least two layers surrounding the core. A five-layer construction that includes two additional layers is one specific type of multi-layer golf ball. Multi-layer balls can offer several advantages due to the complex nature of the physical interaction between the various materials used in the core and the layers.

SUMMARY

Disclosed herein are various golf ball embodiments, and methods for making the golf balls.

In one embodiment, the golf ball comprises:

(a) a core;

(b) an inner mantle layer;

(c) an intermediate mantle layer;

(d) an outer mantle layer; and

(e) at least one cover layer;

wherein the material of each of (a), (b), (c) and (d) has a material flexural modulus and the material flexural modulus increases from the core material (a) to the mantle layers (b), (c) and (d), and wherein within the mantle layers, there is at least one mantle layer that has a material flexural modulus greater than an outwardly adjacent mantle layer.

In another embodiment, a five-piece golf ball comprises:

(a) a core material having a flexural modulus of less than 15 kpsi;

(b) an inner mantle layer material adjacent to the core material, wherein the inner mantle layer material has a flexural modulus of 10-60 kpsi;

(c) an intermediate mantle layer material adjacent to the inner mantle layer material, wherein the intermediate mantle layer material has a flexural modulus of 10-50 kpsi;

(d) an outer mantle layer material adjacent to the intermediate mantle layer material, wherein the outer mantle layer material has a flexural modulus of 30-90 kpsi; and

(e) an outer cover layer material;

wherein the inner mantle layer (b) has a greater flexural modulus than the intermediate mantle layer (c).

In another embodiment, a five-piece golf ball comprises:

(a) a core material having a flexural modulus of less than 15 kpsi;

(b) an inner mantle layer material adjacent to the core material, wherein the inner mantle layer material has a flexural modulus of 2-35 kpsi;

(c) an intermediate mantle layer material adjacent to the inner mantle layer material, wherein the intermediate mantle layer material has a flexural modulus of 30-90 kpsi;

(d) an outer mantle layer material adjacent to the intermediate mantle layer material, wherein the outer mantle layer material has a flexural modulus of 20-60 kpsi; and

(e) an outer cover layer material;

wherein the intermediate mantle layer (c) has a greater flexural modulus than the outer mantle layer (d).

The foregoing will become more apparent from the following detailed description, which proceeds with reference to the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

Referring to the drawing in FIG. **1**, there is illustrated a golf ball **1**, which comprises a solid center or core **2**, formed as a solid body and in the shape of a sphere, an inner mantle layer **3**, disposed on the spherical core, an intermediate mantle layer **4**, disposed on the inner mantle layer **3**, an outer mantle layer **5** disposed on the intermediate mantle layer **4**, and a cover layer **6** disposed on the outer mantle layer **5**. In other words, the intermediate mantle layer **4** is located between the inner mantle layer **3** and the outer mantle layer **5**.

FIG. **2** is a graph of sound pressure level vs. frequency for examples of golf balls according to this application, shown together with conventional golf balls for comparison.

DETAILED DESCRIPTION

For ease of understanding, the following terms used herein are described below in more detail:

The term "core" refers to the elastic center of a golf ball, which may have a unitary construction. Alternatively the core itself may have a layered construction having a spherical "center" and additional "core layers," which such layers usually being made of the same material as the core center.

The term "cover layer" or "cover" refers to any layer or layers of the golf ball adjacent to, and preferably surrounding (partially surrounding or entirely surrounding), the outermost mantle layer. The term "outer cover layer" refers to the outermost cover layer of the golf ball; this is the layer that is directly in contact with paint and/or ink on the surface of the golf ball and on which the dimple pattern is placed. The term outer cover layer as used herein is used interchangeably with the term "outer cover." In some embodiments, the cover may include two or more layers. In these embodiments, the term "inner cover layer" or "inner cover" refers to any cover layer positioned between the outermost mantle layer and the outer cover layer.

The term "mantle layer" or "mantle" refers to any layer(s) in a golf ball disposed between the core and the cover layer(s). The mantle layer may be in the shape of a hollow, thin-skinned sphere that may or may not include inward or outward protrusions (e.g., the intermediate layer may be of substantially the same thickness around its entire curvature). A mantle layer may partially or entirely surround the core. In the case of a ball with two or more mantle layers, the term "inner mantle" or "inner mantle layer" refers to the mantle layer of the ball that is disposed nearest to the core. Again, in the case of a ball with two or more mantle layers, the term "outer mantle" or "outer mantle layer" refers to the mantle layer of the ball that is disposed nearest to the outer cover layer. There may be one or more "intermediate" mantle layers positioned between the inner mantle layer and the outer mantle layer.

The term "bimodal polymer" refers to a polymer comprising two main fractions and more specifically to the form of the polymers molecular weight distribution curve, i.e., the appearance of the graph of the polymer weight fraction as function of its molecular weight. When the molecular weight distribution curves from these fractions are superimposed into the molecular weight distribution curve for the total resulting polymer product, that curve will show two maxima or at least be distinctly broadened in comparison with the curves for the individual fractions. Such a polymer product is called bimodal. It is to be noted here that also the chemical compositions of the two fractions may be different.

Similarly the term "unimodal polymer" refers to a polymer comprising one main fraction and more specifically to the form of the polymer's molecular weight distribution curve, i.e., the molecular weight distribution curve for the total polymer product shows only a single maximum.

A "high acid ionomer" generally refers to an ionomer resin or polymer that includes more than about 16 wt. %, more particularly more than about 19 wt. %, of unsaturated mono- or dicarboxylic acids units based on the weight of resin or polymer.

The term "hydrocarbyl" includes any aliphatic, cycloaliphatic, aromatic, aryl substituted aliphatic, aryl substituted cycloaliphatic, aliphatic substituted aromatic, or cycloaliphatic substituted aromatic groups. The aliphatic or cycloaliphatic groups are preferably saturated. Likewise, the term "hydrocarbyloxy" means a hydrocarbyl group having an oxygen linkage between it and the carbon atom to which it is attached.

The term "(meth)acrylic acid copolymers" refers to copolymers of methacrylic acid and/or acrylic acid.

The term "(meth)acrylate" refers to an ester of methacrylic acid and/or acrylic acid.

The term "partially neutralized" refers to an ionomer with a degree of neutralization of less than 100 percent.

"Prepolymer" refers to any material that can be further processed to form a final polymer material of a manufactured golf ball, such as, by way of example and not limitation, a polymerized or partially polymerized material that can undergo additional processing, such as crosslinking.

The term "polyurea" as used herein refers to materials prepared by reaction of a diisocyanate with a polyamine.

The term "polyurethane" as used herein refers to materials prepared by reaction of a diisocyanate with a polyol.

A "specialty propylene elastomer" includes a thermoplastic propylene-ethylene copolymer composed of a majority amount of propylene and a minority amount of ethylene. These copolymers have at least partial crystallinity due to adjacent isotactic propylene units. Although not bound by any theory, it is believed that the crystalline segments are physical crosslinking sites at room temperature, and at high temperature (i.e., about the melting point), the physical crosslinking is removed and the copolymer is easy to process. According to one embodiment, a specialty propylene elastomer includes at least about 50 mole % propylene co-monomer. Specialty propylene elastomers can also include functional groups such as maleic anhydride, glycidyl, hydroxyl, and/or carboxylic acid. Suitable specialty propylene elastomers include propylene-ethylene copolymers produced in the presence of a metallocene catalyst. More specific examples of specialty propylene elastomers are illustrated below.

A "terpolymeric ionomer" generally refers to ionomers of polymers of general formula, E/X/Y polymer, wherein E is ethylene, X is a C_3 to C_8 α,β ethylenically unsaturated carboxylic acid, such as acrylic or methacrylic acid, and Y is a softening comonomer such as methyl(meth)acrylate or ethyl (meth)acrylate.

A "thermoplastic" is generally defined as a material that is capable of softening or melting when heated and of hardening again when cooled. Thermoplastic polymer chains often are not cross-linked or are lightly crosslinked using a chain extender, but the term "thermoplastic" as used herein may refer to materials that initially act as thermoplastics, such as during an initial extrusion process or injection molding process, but which also may be crosslinked, such as during a compression molding step to form a final structure.

A "thermoset" is generally defined as a material that crosslinks or cures via interaction with a crosslinking or curing agent. Crosslinking may be induced by energy, such as heat (generally above 200° C.), through a chemical reaction (by reaction with a curing agent), or by irradiation. The resulting composition remains rigid when set, and does not soften with heating. Thermosets have this property because the long-chain polymer molecules cross-link with each other to give a rigid structure. A thermoset material cannot be melted and re-molded after it is cured. Thus thermosets do not lend themselves to recycling unlike thermoplastics, which can be melted and re-molded.

The term "thermoplastic polyurethane" refers to a material prepared by reaction of a prepared by reaction of a diisocyanate with a polyol, and optionally addition of a chain extender.

The term "thermoplastic polyurea" refers to a material prepared by reaction of a prepared by reaction of a diisocyanate with a polyamine, with optionally addition of a chain extender.

The term "thermoset polyurethane" refers to a material prepared by reaction of a diisocyanate with a polyol, and a curing agent.

The term "thermoset polyurea" refers to a material prepared by reaction of a diisocyanate with a polyamine, and a curing agent.

A "urethane prepolymer" is the reaction product of diisocyanate and a polyol.

A "urea prepolymer" is the reaction product of a diisocyanate and a polyamine.

The term "unimodal polymer" refers to a polymer comprising one main fraction and more specifically to the form of the polymer's molecular weight distribution curve, i.e., the molecular weight distribution curve for the total polymer product shows only a single maximum.

"Flexural modulus" is the slope of the stress vs. strain curve for a material subjected to a flexural test, and thus has the units of stress divided strain, or force per unit area (e.g., psi). Stated differently, flexural modulus is a measure of how much a sample of a material will bend, within the elastic limit, under a given applied load. Recognized testing standards include ASTM D790 and ISO 178.

The above term descriptions are provided solely to aid the reader, and should not be construed to have a scope less than that understood by a person of ordinary skill in the art or as limiting the scope of the appended claims.

The singular terms "a," "an," and "the" include plural referents unless context clearly indicates otherwise. The word "comprises" indicates "includes." It is further to be understood that all molecular weight or molecular mass values given for compounds are approximate, and are provided for description. The materials, methods, and examples are illustrative only and not intended to be limiting. Unless otherwise indicated, description of components in chemical nomenclature refers to the components at the time of addition to any combination specified in the description, but does not necessarily preclude chemical interactions among the components of a mixture once mixed.

Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component or a value of a process variable is from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 etc., are expressly enumerated in this specification. For values, which have less than one unit difference, one unit is considered to be 0.1, 0.01, 0.001, or 0.0001 as appropriate. Thus, all possible combinations of numerical values between the lowest value and the highest value enumerated herein are said to be expressly stated in this application.

Disclosed herein are golf balls having a mantle construction that can maintain the durability of the golf ball while retaining the soft feel of a low core PGA compression and, as it has been discovered, also meet desired spin characteristics. For example, the core/inner mantle layer/intermediate mantle layer combined construct may have a PGA compression of at least 30, more particularly of at least 40. The phrase "core/inner mantle layer/intermediate mantle layer combined construct" refers to a construct formed from the core, the inner mantle layer and the intermediate mantle layer (i.e., an inner construct located within the outer mantle layer). The PGA compression of this inner combined construct is measured. In certain examples, the PGA compression may be at least 50, more particularly at least 60. In other examples, the PGA compression of the inner combined construct is 30 to 70. The inner combined construct provides extra support for the outer mantle layer to minimize cracking or other damage of the cover layer and/or outer mantle layer. The ball can include more than one inner mantle layer and/or more than one intermediate mantle layer.

With respect to desired spin characteristics, although the general overall configuration of increasing flexural modulus from the core through the various mantle layers tends to produce a golf ball with reduced spin, it has been found that at least one mantle layer with a flexural modulus greater than that of an outwardly positioned mantle layer increases iron spin to a desired degree, yet retains the desired feel and low driver backspin. For example, the intermediate mantle layer can be made to have a higher flexural modulus than an outer mantle layer that is positioned outward of the intermediate mantle layer. As another example, the inner mantle layer can be made to have a higher flexural modulus than the intermediate mantle layer.

The golf balls disclosed herein are at least five-piece golf balls. In other words, the golf balls include at least five separate layers (including the core). The golf ball may include additional mantle layers and/or multiple cover layers.

In certain embodiments, the flexural modulus (FM) of the core and the mantle (M) layers materials follows a selected relationship. One illustrative golf ball satisfies a flexural modulus gradient relationship of: FM(core)<FM(inner M)>FM(intermediate M)<FM(outer M). Another illustrative golf ball satisfies the relationship of: FM(core)<FM(inner M)<FM(intermediate M)>FM(outer M). In other words, the flexural modules generally increases from the core through the mantle except that one of the mantle layers has a flexural modulus that exceeds the flexural modulus of an outwardly adjacent mantle layer. The flexural modulus may be exceeded, for example, by at least 2 kpsi, more particularly by at least 3 kpsi, and most particularly, by 5 kpsi.

In certain embodiments, the material Shore D hardness of each of the core and the layer materials follows the order of the flexural modulus relationship. In other words, for a golf ball where FM(core)<FM(inner M)>FM(intermediate M)<FM(outer M), the hardness (H) follows a similar relationship such that H(core)<H(inner M)>H(intermediate M)<H(outer M). However, there are cases where flexural modulus and material hardness do not follow the same relationship.

In certain embodiments, the "soft feel" of the golf ball (i.e., how the impact of club on ball is transmitted and feels to the golfer) is a function of a specific sound frequency and loudness of the ball. Frequency is a measure of the "pitch" of the sound, and SPL is a measure of the magnitude of sound measured in decibels (dB). Balls can be hit or tested at 30 yard shots for sound and pitch and subsequently this translates into ball feel that the golfer experiences. The combination of a low sound db levels and a low frequency, results in a ball having a soft "feel" to the golfer. For example, the golf ball may have a golf ball frequency of less than 4000 Hz, more particularly less than 3800 Hz, and most particularly less than 3700 Hz. The golf ball may have a sound pressure level, SPL, of less than 92 dB, and more particularly less than 91 dB.

Polymer Components

The core, mantle layer(s) and cover layer(s) may each include one or more of the following polymers.

Such polymers include synthetic and natural rubbers, thermoset polymers such as thermoset polyurethanes and thermoset polyureas, as well as thermoplastic polymers including thermoplastic elastomers such as unimodal ethylene/carboxylic acid copolymers, unimodal ethylene/carboxylic acid/carboxylate terpolymers, bimodal ethylene/carboxylic acid copolymers, bimodal ethylene/carboxylic acid/carboxylate terpolymers, unimodal ionomers, bimodal ionomers, modified unimodal ionomers, modified bimodal ionomers, thermoplastic polyurethanes, thermoplastic polyureas, polyesters, copolyesters, polyamides, copolyamides, polycarbonates, polyolefins, polyphenylene oxide, polyphenylene sulfide, diallyl phthalate polymer, polyimides, polyvinyl chloride, polyamide-ionomer, polyurethane-ionomer, polyvinyl alcohol, polyarylate, polyacrylate, polyphenylene ether, impact-modified polyphenylene ether, polystyrene, high impact polystyrene, acrylonitrile-butadiene-styrene copolymer styrene-acrylonitrile (SAN), acrylonitrile-styrene-acrylonitrile, styrene-maleic anhydride (S/MA) polymer, styrenic copolymer, functionalized styrenic copolymer, functionalized styrenic terpolymer, styrenic terpolymer, cellulose polymer, liquid crystal polymer (LCP), ethylene-propylene-diene terpolymer (EPDM), ethylene-vinyl acetate copolymers (EVA), ethylene-propylene copolymer, ethylene vinyl acetate, polyurea, and polysiloxane and any and all combinations thereof.

More particularly, the synthetic and natural rubber polymers may include the traditional rubber components used in golf ball applications including, both natural and synthetic rubbers, such as cis-1,4-polybutadiene, trans-1,4-polybutadiene, 1,2-polybutadiene, cis-polyisoprene, trans-polyisoprene, polychloroprene, polybutylene, styrene-butadiene rubber, styrene-butadiene-styrene block copolymer and partially and fully hydrogenated equivalents, styrene-isoprene-styrene block copolymer and partially and fully hydrogenated equivalents, nitrile rubber, silicone rubber, and polyurethane, as well as mixtures of these. Polybutadiene rubbers, especially 1,4-polybutadiene rubbers containing at least 40 mol %, and more preferably 80 to 100 mol % of cis-1,4 bonds, are preferred because of their high rebound resilience, moldability, and high strength after vulcanization. The polybutadiene component may be synthesized by using rare earth-based catalysts, nickel-based catalysts, or cobalt-based catalysts, conventionally used in this field. Polybutadiene obtained by using lanthanum rare earth-based catalysts usually employ a combination of a lanthanum rare earth (atomic number of 57 to 71)-compound, but particularly preferred is a neodymium compound.

The 1,4-polybutadiene rubbers have a molecular weight distribution (Mw/Mn) of from about 1.2 to about 4.0, preferably from about 1.7 to about 3.7, even more preferably from about 2.0 to about 3.5, most preferably from about 2.2 to about 3.2. The polybutadiene rubbers have a Mooney viscosity (ML_{1+4}(100° C.)) of from about 20 to about 80, preferably from about 30 to about 70, even more preferably from about 30 to about 60, most preferably from about 35 to about 50. The term "Mooney viscosity" used herein refers in each case to an industrial index of viscosity as measured with a Mooney viscometer, which is a type of rotary plastometer (see JIS K6300). This value is represented by the symbol ML_{1+4}(100° C.), wherein "M" stands for Mooney viscosity, "L" stands for large rotor (L-type), "1+4" stands for a pre-heating time of 1 minute and a rotor rotation time of 4 minutes, and "100° C." indicates that measurement was carried out at a temperature of 100° C.

Examples of 1,2-polybutadienes having differing tacticity, all of which are suitable as unsaturated polymers for use in the presently disclosed compositions, are atactic 1,2-polybutadiene, isotactic 1,2-polybutadiene, and syndiotactic 1,2-polybutadiene. Syndiotactic 1,2-polybutadiene having crystallinity suitable for use as an unsaturated polymer in the presently disclosed compositions are polymerized from a 1,2-addition of butadiene. The presently disclosed golf balls may include syndiotactic 1,2-polybutadiene having crystallinity and greater than about 70% of 1,2-bonds, more preferably greater than about 80% of 1,2-bonds, and most preferably greater than about 90% of 1,2-bonds. Also, the 1,2-polybutadiene may have a mean molecular weight between about 10,000 and about 350,000, more preferably between about 50,000 and about 300,000, more preferably between about 80,000 and about 200,000, and most preferably between about 10,000 and about 150,000. Examples of suitable syndiotactic 1,2-polybutadienes having crystallinity suitable for use in golf balls are sold under the trade names RB810, RB820, and RB830 by JSR Corporation of Tokyo, Japan. These have more than 90% of 1,2 bonds, a mean molecular weight of approximately 120,000, and crystallinity between about 15% and about 30%.

Other synthetic rubber polymers for use in the golf balls of the present invention include polyalkenamers as described, for example, in US-2006-0166762-A1, which is incorporated herein by reference in its entirety. Polyalkenamers may be prepared by ring opening metathesis polymerization of one or more cycloalkenes in the presence of organometallic catalysts as described in U.S. Pat. Nos. 3,492,245 and 3,804,803, the entire contents of both of which are herein incorporated by reference. Examples of suitable polyalkenamer rubbers are polymer of one or more cycloalkenes having from 4-20, ring carbon atoms.

Examples of suitable polyalkenamer rubbers are polypentenamer rubber, polyheptenamer rubber, polyoctenamer rubber, polydecenamer rubber and polydodecenamer rubber. For further details concerning polyalkenamer rubber, see *Rubber Chem. & Tech.*, Vol. 47, page 511-596, 1974, which is incorporated herein by reference. Polyoctenamer rubbers are commercially available from Huls AG of Marl, Germany, and through its distributor in the U.S., Creanova Inc. of Somerset, N.J., and sold under the trademark VESTENAMER®. Two grades of the VESTENAMER® trans-polyoctenamer are commercially available: VESTENAMER 8012 designates a material having a trans-content of approximately 80% (and a cis-content of 20%) with a melting point of approximately 54° C.; and VESTENAMER 6213 designates a material having a trans-content of approximately 60% (cis-content of 40%) with a melting point of approximately 30° C. Both of these polymers have a double bond at every eighth carbon atom in the ring.

The polyalkenamer rubbers used in the present disclosure exhibit excellent melt processability above their sharp melting temperatures and exhibit high miscibility with various rubber additives as a major component without deterioration of crystallinity which in turn facilitates injection molding. Thus, unlike synthetic polybutadiene rubbers typically used in golf ball core preparation, injection molded parts of polyalkenamer-based compounds can be prepared which, in addition, can also be partially or fully crosslinked at elevated temperature. The crosslinked polyalkenamer compounds are highly elastic, and their mechanical and physical properties can be easily modified by adjusting the formulation.

The polyalkenamer composition surprisingly exhibits superior characteristics over a broad spectrum of properties that relate to the effectiveness of a composition for use in the SCR of the golf balls of the present invention. For example, the composition exhibits superior impact durability and Coefficient of Restitution (COR) in a pre-determined hardness range (e.g., a hardness Shore D of from about 15 to about 85, preferably from about 40 to about 80, and more preferably from about 40 to about 75. More particularly, the compositions disclosed herein exhibit excellent hardness adjustment without significantly compromising COR or processability.

If a polyalkenamer rubber is present, the polyalkenamer rubber preferably contains from about 50 to about 99, preferably from about 60 to about 99, more preferably from about 65 to about 99, even more preferably from about 70 to about 90 percent of its double bonds in the trans-configuration. The preferred form of the polyalkenamer has a trans content of approximately 80%, however, compounds having other ratios of the cis- and trans-isomeric forms of the polyalkenamer can also be obtained by blending available products for use in making the composition.

The polyalkenamer rubber has a molecular weight (as measured by GPC) from about 10,000 to about 300,000, preferably from about 20,000 to about 250,000, more preferably from about 30,000 to about 200,000, even more preferably from about 50,000 to about 150,000.

The polyalkenamer rubber has a degree of crystallization (as measured by DSC secondary fusion) from about 5 to about 70, preferably from about 6 to about 50, more preferably from about from 6.5 to about 50%, even more preferably from about from 7 to about 45%.

The polyalkenamer rubbers may also be blended within other polymers and an especially preferred blend is that of a polyalkenamer and a polyamide. A more complete description of the polyalkenamer rubbers are disclosed in U.S. Pat. No. 7,528,196 and co-pending U.S. application Ser. No. 12/415,522, filed on Mar. 31, 2009, both in the name of Hyun Kim et al., the entire contents of both of which are hereby incorporated by reference.

There are a number of applications of polyalkenamer blends in game balls of various kinds. For example, U.S. Pat. No. 5,460,367 describes a pressureless tennis ball comprising a blend of trans-polyoctenamer rubber and natural rubber or other synthetic rubbers, e.g. cis-1,4-polybutadiene, trans-polybutadiene, polyisoprene, styrene-butadiene rubber, ethylene-propylene rubber or an ethylene-propylene-diene rubber (EPDM).

Also, U.S. Pat. No. 4,792,141 describes a golf ball comprising a core and a cover wherein the cover is formed from a composition comprising about 97 to about 60 parts by weight and about 3 to about 40 parts by weight polyoctenylene rubber based on 100 parts by weight polymer in the composition. This patent also discloses that using more than about 40 parts by weight of polyoctenylene based on 100 parts by weight polymer in the composition has been found to produce deleterious effects.

More preferably, the polyalkenamer rubber is a polymer prepared by polymerization of cyclooctene to form a trans-polyoctenamer rubber as a mixture of linear and cyclic macromolecules.

Any crosslinking or curing system typically used for crosslinking may be used to crosslink the synthetic rubber compositions used to make the golf balls of the present invention. Satisfactory crosslinking systems are based on sulfur-, peroxide-, azide-, maleimide- or resin-vulcanization agents, which may be used in conjunction with a vulcanization accelerator. Examples of satisfactory crosslinking system components are zinc oxide, sulfur, organic peroxide, azo compounds, magnesium oxide, benzothiazole sulfenamide accelerator, benzothiazyl disulfide, phenolic curing resin, m-phenylene bis-maleimide, thiuram disulfide and dipentamethylene-thiuram hexasulfide.

More preferable cross-linking agents include peroxides, sulfur compounds, as well as mixtures of these. Non-limiting examples of suitable cross-linking agents include primary, secondary, or tertiary aliphatic or aromatic organic peroxides. Peroxides containing more than one peroxy group can be used, such as 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane and 1,4-di-(2-tert-butyl peroxyisopropyl)benzene. Both symmetrical and asymmetrical peroxides can be used, for example, tert-butyl perbenzoate and tert-butyl cumyl peroxide. Peroxides incorporating carboxyl groups also are suitable. The decomposition of peroxides used as cross-linking agents in the disclosed compositions can be brought about by applying thermal energy, shear, irradiation (e.g., ultra violet-active agents or electron beam-active agents), reaction with other chemicals, or any combination of these. Both homolytically and heterolytically decomposed peroxide can be used. Non-limiting examples of suitable peroxides include: diacetyl peroxide; di-tert-butyl peroxide; dibenzoyl peroxide; dicumyl peroxide; 2,5-dimethyl-2,5-di(benzoylperoxy)hexane; 1,4-bis-(t-butylperoxyisopropyl)benzene; t-butylperoxybenzoate; 2,5-dimethyl-2,5-di-(t-butylperoxy)hexyne-3, such as Trigonox 145-45B, marketed by Akrochem Corp. of Akron, Ohio; 1,1-bis(t-butylperoxy)-3,3,5 tri-methylcyclohexane, such as Varox 231-XL, marketed by R.T. Vanderbilt Co., Inc. of Norwalk, Conn.; and di-(2,4-dichlorobenzoyl) peroxide.

The cross-linking agents can be blended in total amounts of about 0.01 part to about 5 parts, more preferably about 0.05 part to about 4 parts, and most preferably about 0.1 part to about 2 parts, by weight of the cross-linking agents per 100 parts by weight of the polymer-containing composition.

In a further embodiment, the cross-linking agents can be blended in total amounts of about 0.1 part to about 10 parts, more preferably about 0.4 part to about 6 parts, and most preferably about 0.8 part to about 4 parts, by weight of the cross-linking agents per 100 parts by weight of the polymer-containing composition. The crosslinking agent(s) may be mixed directly into or with the synthetic rubber compositions, or the crosslinking agent(s) may be pre-mixed with the synthetic rubber component to form a concentrated compound prior to subsequent compounding with the bulk of the synthetic rubber compositions used in the present invention.

Each peroxide cross-linking agent has a characteristic decomposition temperature at which 50% of the cross-linking agent has decomposed when subjected to that temperature for a specified time period ($t_{1/2}$). For example, 1,1-bis-(t-butylperoxy)-3,3,5-tri-methylcyclohexane at $t_{1/2}$=0.1 hour has a decomposition temperature of 138° C. and 2,5-dimethyl-2,5-di-(t-butylperoxy)hexyne-3 at $t_{1/2}$=0.1 hour has a decomposition temperature of 182° C. Two or more cross-linking agents having different characteristic decomposition temperatures at the same $t_{1/2}$ may be blended in the composition. For example, where at least one cross-linking agent has a first characteristic decomposition temperature less than 150° C., and at least one cross-linking agent has a second characteristic decomposition temperature greater than 150° C., the composition weight ratio of the at least one cross-linking agent having the first characteristic decomposition temperature to the at least one cross-linking agent having the second characteristic decomposition temperature can range from 5:95 to 95:5, or more preferably from 10:90 to 50:50.

Besides the use of chemical cross-linking agents, exposure of the polymer-containing composition to radiation also can serve as a cross-linking agent. Radiation can be applied to the polymer-containing composition by any known method, including using microwave or gamma radiation, or an electron beam device. Additives may also be used to improve radiation-induced crosslinking of the polymer-containing composition.

The synthetic and natural rubbers may also be blended with a co-cross-linking agent, which may be a metal salt of an unsaturated carboxylic acid. Examples of these include zinc and magnesium salts of unsaturated fatty acids having 3 to 8 carbon atoms, such as acrylic acid, methacrylic acid, maleic acid, and fumaric acid, palmitic acid with the zinc salts of acrylic and methacrylic acid being most preferred. The unsaturated carboxylic acid metal salt can be blended in the polymer-containing composition either as a preformed metal salt, or by introducing an α,β-unsaturated carboxylic acid and a metal oxide or hydroxide into the polymer-containing composition, and allowing them to react to form the metal salt. The unsaturated carboxylic acid metal salt can be blended in any desired amount, but preferably in amounts of about 1 part to about 100 parts by weight of the unsaturated carboxylic acid per 100 parts by weight of the polymer-containing composition.

The synthetic and natural rubbers may also be blended with one or more of the so-called "peptizers."

The peptizer preferably comprises an organic sulfur compound and/or its metal or non-metal salt. Examples of such organic sulfur compounds include thiophenols, such as pentachlorothiophenol, 4-butyl-o-thiocresol, 4 t-butyl-p-thiocresol, and 2-benzamidothiophenol; thiocarboxylic acids, such as thiobenzoic acid; 4,4' dithio dimorpholine; and, sulfides, such as dixylyl disulfide, dibenzoyl disulfide; dibenzothiazyl disulfide; di(pentachlorophenyl)disulfide; dibenzamido diphenyldisulfide (DBDD), and alkylated phenol sulfides, such as VULTAC marketed by Atofina Chemicals, Inc. of Philadelphia, Pa. Preferred organic sulfur compounds include pentachlorothiophenol, and dibenzamido diphenyldisulfide. Another suitable peptizer is 2,3,5,6-tetrachloro-4-pyridinethiol (TCPT).

Examples of the metal salt of an organic sulfur compound include sodium, potassium, lithium, magnesium calcium, barium, cesium and zinc salts of the above-mentioned thiophenols and thiocarboxylic acids, with the zinc salt of pentachlorothiophenol being most preferred.

Examples of the non-metal salt of an organic sulfur compound include ammonium salts of the above-mentioned thiophenols and thiocarboxylic acids wherein the ammonium cation has the general formula $[NR^1R^2R^3R^4]^+$ where R^1, R^2, R^3 and R^4 are selected from the group consisting of hydrogen, a C_1-C_{20} aliphatic, cycloaliphatic or aromatic moiety, and any and all combinations thereof, with the most preferred being the NH_4^+-salt of pentachlorothiophenol.

Additional peptizers include aromatic or conjugated peptizers comprising one or more heteroatoms, such as nitrogen, oxygen and/or sulfur. More typically, such peptizers are heteroaryl or heterocyclic compounds having at least one heteroatom, and potentially plural heteroatoms, where the plural heteroatoms may be the same or different. Such peptizers include peptizers such as an indole peptizer, a quinoline peptizer, an isoquinoline peptizer, a pyridine peptizer, purine peptizer, a pyrimidine peptizer, a diazine peptizer, a pyrazine peptizer, a triazine peptizer, a carbazole peptizer, or combinations of such peptizers.

Suitable peptizers also may include one or more additional functional groups, such as halogens, particularly chlorine; a sulfur-containing moiety exemplified by thiols, where the functional group is sulfhydrl (—SH), thioethers, where the functional group is —SR, disulfides, (R_1S—SR_2), etc.; and combinations of functional groups. Such peptizers are more fully disclosed in copending U.S. Provisional Patent Application No. 60/752,475 filed on Dec. 20, 2005, and U.S. patent application Ser. No. 11/639,871, filed on Dec. 15, 2006, in the name of Hyun Kim et al, the entire contents of which are herein incorporated by reference. A most preferred example is a pyridine peptizer that also includes a chlorine functional group and a thiol functional group such as 2,3,5,6-tetrachloro-4-pyridinethiol (TCPT).

The peptizer, if employed in the golf balls, is present in an amount of from about 0.01 to about 10, preferably of from about 0.05 to about 7, more preferably of from about 0.1 to about 5 parts by weight per 100 parts by weight of the polymer-containing composition.

The synthetic and natural rubbers may also comprise one or more accelerators of one or more classes. Accelerators are added to an unsaturated polymer to increase the vulcanization rate and/or decrease the vulcanization temperature. Accelerators can be of any class known for rubber processing including mercapto-, sulfenamide-, thiuram, dithiocarbamate, dithiocarbamyl-sulfenamide, xanthate, guanidine, amine, thiourea, and dithiophosphate accelerators. Specific commercial accelerators include 2-mercaptobenzothiazole and its metal or non-metal salts, such as Vulkacit Mercapto C, Mercapto MGC, Mercapto ZM-5, and ZM marketed by Bayer AG of Leverkusen, Germany, Nocceler M, Nocceler MZ, and Nocceler M-60 marketed by Ouchisinko Chemical Industrial Company, Ltd. of Tokyo, Japan, and MBT and ZMBT marketed by Akrochem Corporation of Akron, Ohio. A more complete list of commercially available accelerators is given in *The Vanderbilt Rubber Handbook: 13th Edition* (1990, R.T. Vanderbilt Co.), pp. 296-330, in *Encyclopedia of Polymer Science and Technology*, Vol. 12 (1970, John Wiley & Sons), pp. 258-259, and in *Rubber Technology Handbook* (1980, Hanser/Gardner Publications), pp. 234-236. Preferred accelerators include 2-mercaptobenzothiazole (MBT) and its salts.

The polymer-containing composition can further incorporate from about 0.01 part to about 10 parts by weight of the accelerator per 100 parts by weight of the polymer-containing composition. More preferably, the ball composition can further incorporate from about 0.02 part to about 5 parts, and most preferably from about 0.03 part to about 1.5 parts, by weight of the accelerator per 100 parts by weight of the polymer.

More specific examples of olefinic thermoplastic elastomers include metallocene-catalyzed polyolefins, ethylene-octene copolymer, ethylene-butene copolymer, and ethylene-propylene copolymers all with or without controlled tacticity as well as blends of polyolefins having ethyl-propylene-non-conjugated diene terpolymer, rubber-based copolymer, and dynamically vulcanized rubber-based copolymer. Examples of these include products sold under the trade names SANTOPRENE, DYTRON, VISAFLEX, and VYRAM by Advanced Elastomeric Systems of Houston, Tex., and SARLINK by DSM of Haarlen, the Netherlands.

Examples of rubber-based thermoplastic elastomers include multiblock rubber-based copolymers, particularly those in which the rubber block component is based on butadiene, isoprene, or ethylene/butylene. The non-rubber repeating units of the copolymer may be derived from any suitable monomers, including meth(acrylate) esters, such as methyl methacrylate and cyclohexylmethacrylate, and vinyl arylenes, such as styrene. Examples of styrenic copolymers are resins manufactured by Kraton Polymers (formerly of Shell Chemicals) under the trade names KRATON D (for styrene-butadiene-styrene and styrene-isoprene-styrene types) and KRATON G (for styrene-ethylene-butylene-styrene and styrene-ethylene-propylene-styrene types) and Kuraray under the trade name SEPTON. Examples of randomly distributed styrenic polymers include paramethylstyrene-isobutylene (isobutene) copolymers developed by ExxonMobil Chemical Corporation and styrene-butadiene random copolymers developed by Chevron Phillips Chemical Corp.

Examples of copolyester thermoplastic elastomers include polyether ester block copolymers, polylactone ester block copolymers, and aliphatic and aromatic dicarboxylic acid copolymerized polyesters. Polyether ester block copolymers are copolymers comprising polyester hard segments polymerized from a dicarboxylic acid and a low molecular weight diol, and polyether soft segments polymerized from an alkylene glycol having 2 to 10 atoms. Polylactone ester block copolymers are copolymers having polylactone chains instead of polyether as the soft segments discussed above for polyether ester block copolymers. Aliphatic and aromatic dicarboxylic copolymerized polyesters are copolymers of an acid component selected from aromatic dicarboxylic acids, such as terephthalic acid and isophthalic acid, and aliphatic acids having 2 to 10 carbon atoms with at least one diol component, selected from aliphatic and alicyclic diols having 2 to 10 carbon atoms. Blends of aromatic polyester and aliphatic polyester also may be used for these. Examples of these include products marketed under the trade names HYTREL by E.I. DuPont de Nemours & Company, and SKYPEL by S.K. Chemicals of Seoul, South Korea.

Examples of other suitable thermoplastic elastomers include those having functional groups, such as carboxylic acid, maleic anhydride, glycidyl, norbonene, and hydroxyl functionalities. An example of these includes a block polymer having at least one polymer block A comprising an aromatic vinyl compound and at least one polymer block B comprising a conjugated diene compound, and having a hydroxyl group at the terminal block copolymer, or its hydrogenated product. An example of this polymer is sold under the trade name SEPTON HG-252 by Kuraray Company of Kurashiki, Japan. Other examples of these include: maleic anhydride functionalized triblock copolymer consisting of polystyrene end blocks and poly(ethylene/butylene), sold under the trade name KRATON FG 1901X by Shell Chemical Company; maleic anhydride modified ethylene-vinyl acetate copolymer, sold under the trade name FUSABOND by E.I. DuPont de Nemours & Company; ethylene-isobutyl acrylate-methacrylic acid terpolymer, sold under the trade name NUCREL by E.I. DuPont de Nemours & Company; ethylene-ethyl acrylate-methacrylic anhydride terpolymer, sold under the trade name BONDINE AX 8390 and 8060 by Sumitomo Chemical Industries; brominated styrene-isobutylene copolymers sold under the trade name BROMO XP-50 by Exxon Mobil Corporation; and resins having glycidyl or maleic anhydride functional groups sold under the trade name LOTADER by Elf Atochem of Puteaux, France.

Another example of a polymer for making any of the core, mantle layer(s) or cover layer(s) is blend of a polyamide (which may be a polyamide as described above) with a functional polymer modifier of the polyamide. The functional polymer modifier of the polyamide can include copolymers or terpolymers having a glycidyl group, hydroxyl group, maleic anhydride group or carboxylic group, collectively referred to as functionalized polymers. These copolymers and terpolymers may comprise an α-olefin. Examples of suitable α-olefins include ethylene, propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-petene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicocene, 1-dococene, 1-tetracocene, 1-hexacocene, 1-octacocene, and 1-triacontene. One or more of these α-olefins may be used.

Examples of suitable glycidyl groups in copolymers or terpolymers in the polymeric modifier include esters and ethers of aliphatic glycidyl, such as allylglycidylether, vinylglycidylether, glycidyl maleate and itaconatem glycidyl acrylate and methacrylate, and also alicyclic glycidyl esters and ethers, such as 2-cyclohexene-1-glycidylether, cyclohexene-4,5 diglyxidylcarboxylate, cyclohexene-4-glycidyl carobxylate, 5-norboenene-2-methyl-2-glycidyl carboxylate, and endocis-bicyclo(2,2,1)-5-heptene-2,3-diglycidyl dicarboxylate. These polymers having a glycidyl group may comprise other monomers, such as esters of unsaturated carboxylic acid, for example, alkyl(meth)acrylates or vinyl esters of unsaturated carboxylic acids. Polymers having a glycidyl group can be obtained by copolymerization or graft polymerization with homopolymers or copolymers.

Examples of suitable terpolymers having a glycidyl group include LOTADER AX8900 and AX8920, marketed by Atofina Chemicals, ELVALOY marketed by E.I. Du Pont de Nemours & Co., and REXPEARL marketed by Nippon Petrochemicals Co., Ltd. Additional examples of copolymers comprising epoxy monomers and which are suitable for use within the scope of the present invention include styrene-butadiene-styrene block copolymers in which the polybutadiene block contains epoxy group, and styrene-isoprene-styrene block copolymers in which the polyisoprene block contains epoxy. Commercially available examples of these epoxy functional copolymers include ESBS A1005, ESBS A1010, ESBS A1020, ESBS AT018, and ESBS AT019, marketed by Daicel Chemical Industries, Ltd.

Examples of polymers or terpolymers incorporating a maleic anhydride group suitable for use within the scope of the present invention include maleic anhydride-modified ethylene-propylene copolymers, maleic anhydride-modified ethylene-propylene-diene terpolymers, maleic anhydride-modified polyethylenes, maleic anhydride-modified polypropylenes, ethylene-ethylacrylate-maleic anhydride terpolymers, and maleic anhydride-indene-styrene-cumarone polymers. Examples of commercially available copolymers incorporating maleic anhydride include: BONDINE, marketed by Sumitomo Chemical Co., such as BONDINE AX8390, an ethylene-ethyl acrylate-maleic anhydride terpolymer having a combined ethylene acrylate and maleic anhydride content of 32% by weight, and BONDINE TX TX8030, an ethylene-ethyl acrylate-maleic anhydride terpolymer having a combined ethylene acrylate and maleic anhydride content of 15% by weight and a maleic anhydride content of 1% to 4% by weight; maleic anhydride-containing LOTADER 3200, 3210, 6200, 8200, 3300, 3400, 3410, 7500, 5500, 4720, and 4700, marketed by Atofina Chemicals; EXXELOR VA 1803, a maleic anyhydride-modified ethylene-propylene copolymer having a maleic anyhydride content of 0.7% by weight, marketed by Exxon Chemical Co.; and KRATON FG 1901X, a maleic anhydride functionalized triblock copolymer having polystyrene endblocks and poly(ethylene/butylene) midblocks, marketed by Shell Chemical.

Preferably the functional polymer component for blending with a polyamide is a maleic anhydride grafted polymer, preferably a maleic anhydride grafted polyolefin (for example, Exxellor VA1803).

Styrenic block copolymers are copolymers of styrene with butadiene, isoprene, or a mixture of the two. Additional unsaturated monomers may be added to the structure of the styrenic block copolymer as needed for property modification of the resulting SBC/urethane copolymer. The styrenic block copolymer can be a diblock or a triblock styrenic polymer. Examples of such styrenic block copolymers are described in, for example, U.S. Pat. No. 5,436,295 to Nishikawa et al. The styrenic block copolymer can have any known molecular weight for such polymers, and it can possess a linear, branched, star, dendrimeric or combination molecular structure. The styrenic block copolymer can be unmodified by functional groups, or it can be modified by hydroxyl group, carboxyl group, or other functional groups, either in its chain structure or at one or more terminus. The styrenic block copolymer can be obtained using any common process for manufacture of such polymers. The styrenic block copolymers also may be hydrogenated using well-known methods to obtain a partially or fully saturated diene monomer block.

Other preferred materials suitable for use in the presently disclosed golf balls include polyester thermoplastic elastomers marketed under the tradename SKYPEL™ by SK Chemicals of South Korea, or diblock or triblock copolymers marketed under the tradename SEPTON™ by Kuraray Corporation of Kurashiki, Japan, and KRATON™ by Kraton Polymers Group of Companies of Chester, United Kingdom. For example, SEPTON HG 252 is a triblock copolymer, which has polystyrene end blocks and a hydrogenated polyisoprene midblock and has hydroxyl groups at the end of the polystyrene blocks. HG-252 is commercially available from Kuraray America Inc. (Houston, Tex.).

Another preferred material which may be used as a component of the cover layer and/or mantle layers of the golf balls of the present invention is the family of thermoplastic or thermoset polyurethanes or polyureas, which are typically are prepared by reacting a diisocyanate with a polyol (in the case of polyurethanes) or with a polyamine (in the case of a polyurea). Thermoplastic polyurethanes or polyureas may consist solely of this initial mixture or may be further combined with a chain extender to vary properties such as hardness of the thermoplastic. Thermoset polyurethanes or polyureas typically are formed by the reaction of a diisocyanate and a polyol or polyamine respectively, and an additional crosslinking agent to crosslink or cure the material to result in a thermoset.

In what is known as a one-shot process, the three reactants, diisocyanate, polyol or polyamine, and optionally a chain extender or a curing agent, are combined in one step. Alternatively, a two-step process may occur in which the first step involves reacting the diisocyanate and the polyol (in the case of polyurethane) or the polyamine (in the case of a polyurea) to form a so-called prepolymer, to which can then be added either the chain extender or the curing agent. This procedure is known as the prepolymer process.

In addition, although depicted as discrete component packages as above, it is also possible to control the degree of crosslinking, and hence the degree of thermoplastic or thermoset properties in a final composition, by varying the stoichiometry not only of the diisocyanate-to-chain extender or diisocyanate-to-curing agent ratio, but also the initial diisocyanate-to-polyol or diisocyanate-to-polyamine ratio. Of course in the prepolymer process, the initial diisocyanate-to-polyol or polyamine ratio is fixed on selection of the required prepolymer.

In addition to discrete thermoplastic or thermoset materials, it also is possible to modify a thermoplastic polyurethane or polyurea composition by introducing materials in the composition that undergo subsequent curing after molding the thermoplastic to provide properties similar to those of a thermoset. A so called post-curable polyurea or polyurethane. For example, Kim in U.S. Pat. No. 6,924,337, the entire contents of which are hereby incorporated by reference, discloses a thermoplastic urethane or urea composition optionally comprising chain extenders and further comprising a peroxide or peroxide mixture, which can then undergo post curing to result in a thermoset.

Also, Kim et al. in U.S. Pat. No. 6,939,924, the entire contents of which are hereby incorporated by reference, discloses a thermoplastic urethane or urea composition, optionally also comprising chain extenders, that is prepared from a diisocyanate and a modified or blocked diisocyanate which unblocks and induces further cross linking post extrusion. The modified isocyanate preferably is selected from the group consisting of: isophorone diisocyanate (IPDI)-based uretdione-type crosslinker; a combination of a uretdione adduct of IPDI and a partially e-caprolactam-modified IPDI; a combination of isocyanate adducts modified by e-caprolactam and a carboxylic acid functional group; a caprolactam-modified Desmodur diisocyanate; a Desmodur diisocyanate having a 3,5-dimethylpyrazole modified isocyanate; or mixtures of these.

Finally, Kim et al. in U.S. Pat. No. 7,037,985 B2, the entire contents of which are hereby incorporated by reference, discloses thermoplastic urethane or urea compositions further comprising a reaction product of a nitroso compound and a diisocyanate or a polyisocyanate. The nitroso reaction product has a characteristic temperature at which it decomposes to regenerate the nitroso compound and diisocyanate or polyisocyanate. Thus, by judicious choice of the post-processing temperature, further crosslinking can be induced in the originally thermoplastic composition to provide thermoset-like properties.

Any isocyanate available to one of ordinary skill in the art is suitable for use in the various thermoplastic, thermoset or post-cured polyurethane and/or polyurea compositions for use in the golf balls of the present invention. Such isocyanates include, but are not limited to, aliphatic, cycloaliphatic, aromatic aliphatic, aromatic, any derivatives thereof, and combinations of these compounds having two or more isocyanate (NCO) groups per molecule. As used herein, aromatic aliphatic compounds should be understood as those containing an aromatic ring, wherein the isocyanate group is not directly bonded to the ring. One example of an aromatic aliphatic compound is a tetramethylene diisocyanate (TMXDI). The isocyanates may be organic polyisocyanate-terminated prepolymers, low free isocyanate prepolymer, and mixtures thereof. The isocyanate-containing reactable component also may include any isocyanate-functional monomer, dimer, trimer, or polymeric adduct thereof, prepolymer, quasi-prepolymer, or mixtures thereof. Isocyanate-functional compounds may include monoisocyanates or polyisocyanates that include any isocyanate functionality of two or more.

Suitable isocyanate-containing components include diisocyanates having the generic structure: O═C═N—R—N═C═O, where R preferably is a cyclic, aromatic, or linear or branched hydrocarbon moiety containing from about 1 to about 50 carbon atoms. The isocyanate also may contain one or more cyclic groups or one or more phenyl groups. When multiple cyclic or aromatic groups are present, linear and/or branched hydrocarbons containing from about 1 to about 10 carbon atoms can be present as spacers between the cyclic or aromatic groups. In some cases, the cyclic or aromatic group(s) may be substituted at the 2-, 3-, and/or 4-positions, or at the ortho-, meta-, and/or para-positions, respectively. Substituted groups may include, but are not limited to, halogens, primary, secondary, or tertiary hydrocarbon groups, or a mixture thereof.

Examples of isocyanates that can be used with the present invention include, but are not limited to, substituted and isomeric mixtures including 2,2'-, 2,4'-, and 4,4'-diphenylmethane diisocyanate (MDI); 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI); toluene diisocyanate (TDI); polymeric MDI; carbodiimide-modified liquid 4,4'-diphenylmethane diisocyanate; para-phenylene diisocyanate (PPDI); meta-phenylene diisocyanate (MPDI); triphenyl methane-4,4'- and triphenyl methane-4,4"-triisocyanate; naphthylene-1,5-diisocyanate; 2,4'-, 4,4'-, and 2,2-biphenyl diisocyanate; polyphenylene polymethylene polyisocyanate (PMDI) (also known as polymeric PMDI); mixtures of MDI and PMDI; mixtures of PMDI and TDI; ethylene diisocyanate; propylene-1,2-diisocyanate; trimethylene diisocyanate; butylenes diisocyanate; bitolylene diisocyanate; tolidine diisocyanate; tetramethylene-1,2-diisocyanate; tetramethylene-1,3-diisocyanate; tetramethylene-1,4-diisocyanate; pentamethylene diisocyanate; 1,6-hexamethylene diisocyanate (HDI); octamethylene diisocyanate; decamethylene diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; dicyclohexylmethane diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,2-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; diethylidene diisocyanate; methylcyclohexylene diisocyanate (HTDI); 2,4-methylcyclohexane diisocyanate; 2,6-methylcyclohexane diisocyanate; 4,4'-dicyclohexyl diisocyanate; 2,4'-dicyclohexyl diisocyanate; 1,3,5-cyclohexane triisocyanate; isocyanatomethylcyclohexane isocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isocyanatoethylcyclohexane isocyanate; bis(isocyanatomethyl)-cyclohexane diisocyanate; 4,4'-bis(isocyanatomethyl) dicyclohexane; 2,4'-bis(isocyanatomethyl)dicyclohexane; isophorone diisocyanate (IPDI); dimeryl diisocyanate, dodecane-1,12-diisocyanate, 1,10-decamethylene diisocyanate, cyclohexylene-1,2-diisocyanate, 1,10-decamethylene diisocyanate, 1-chlorobenzene-2,4-diisocyanate, furfurylidene diisocyanate, 2,4,4-trimethyl hexamethylene diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate, dodecamethylene diisocyanate, 1,3-cyclopentane diisocyanate, 1,3-cyclohexane diisocyanate, 1,3-cyclobutane diisocyanate, 1,4-cyclohexane diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), 4,4'-methylenebis(phenyl isocyanate), 1-methyl-2,4-cyclohexane diisocyanate, 1-methyl-2,6-cyclohexane diisocyanate, 1,3-bis(isocyanato-methyl)cyclohexane, 1,6-diisocyanato-2,2,4,4-tetra-methylhexane, 1,6-diisocyanato-2,4,4-tetra-trimethylhexane, trans-cyclohexane-1,4-diisocyanate, 3-isocyanato-methyl-3,5,5-trimethylcyclohexyl isocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, cyclohexyl isocyanate, dicyclohexylmethane 4,4'-diisocyanate, 1,4-bis(isocyanatomethyl)cyclohexane, m-phenylene diisocyanate, m-xylylene diisocyanate, m-tetramethylxylylene diisocyanate, p-phenylene diisocyanate, p,p'-biphenyl diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, 3,3'-diphenyl-4,4'-biphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate, 1,5-naphthalene diisocyanate, 4-chloro-1,3-phenylene diisocyanate, 1,5-tetrahydronaphthalene diisocyanate, metaxylene diisocyanate, 2,4-toluene diisocyanate, 2,4'-diphenylmethane diisocyanate, 2,4-chlorophenylene diisocyanate, 4,4'-diphenylmethane diisocyanate, p,p'-diphenylmethane diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 2,2-diphenylpropane-4,4'-diisocyanate, 4,4'-toluidine diisocyanate, dianidine diisocyanate, 4,4'-diphenyl ether diisocyanate, 1,3-xylylene diisocyanate, 1,4-naphthylene diisocyanate, azobenzene-4,4'-diisocyanate, diphenyl sulfone-4,4'-diisocyanate, triphenylmethane 4,4',4"-triisocyanate, isocyanatoethyl methacrylate, 3-isopropenyl-α,α-dimethylbenzyl-isocyanate, dichlorohexamethylene diisocyanate, ω,ω'-diisocyanato-1,4-diethylbenzene, polymethylene polyphenylene polyisocyanate, isocyanurate modified compounds, and carbodiimide modified compounds, as well as biuret modified compounds of the above polyisocyanates. These isocyanates may be used either alone or in combination. These combination isocyanates include triisocyanates, such as biuret of hexamethylene diisocyanate and triphenylmethane triisocyanates, and polyisocyanates, such as polymeric diphenylmethane diisocyanate.triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate (TMDI); 4,4'-dicyclohexylmethane diisocyanate ($H_{12}MDI$); 2,4-hexahydrotoluene diisocyanate; 2,6-hexahydrotoluene diisocyanate; 1,2-, 1,3-, and 1,4-phenylene diisocyanate; aromatic aliphatic isocyanate, such as 1,2-, 1,3-, and 1,4-xylene diisocyanate; meta-tetramethylxylene diisocyanate (m-TMXDI); para-tetramethylxylene diisocyanate (p-TMXDI); trimerized isocyanurate of any polyisocyanate, such as isocyanurate of toluene diisocyanate, trimer of diphenylmethane diisocyanate, trimer of tetramethylxylene diisocyanate, isocyanurate of hexamethylene diisocyanate, and mixtures thereof, dimerized uretdione of any polyisocyanate, such as uretdione of toluene diisocyanate, uretdione of hexamethylene diisocyanate, and mixtures thereof; modified polyisocyanate derived from the above isocyanates and polyisocyanates; and mixtures thereof.

Any polyol now known or hereafter developed is suitable for use in the thermoplastic, thermoset or post-cured polyurethane and/or polyurea compositions according to the invention. Polyols suitable for use in the present invention include, but are not limited to, polyester polyols, polyether polyols, polycarbonate polyols and polydiene polyols such as polybutadiene polyols.

Any polyamine available to one of ordinary skill in the polyurethane art is suitable for use in the thermoplastic, thermoset or post-cured polyurethane and/or polyurea compositions according to the invention. Polyamines suitable for use in the compositions of the present invention include, but are not limited to, amine-terminated compounds typically are selected from amine-terminated hydrocarbons, amine-terminated polyethers, amine-terminated polyesters, amine-terminated polycaprolactones, amine-terminated polycarbonates, amine-terminated polyamides, and mixtures thereof. The amine-terminated compound may be a polyether amine selected from polytetramethylene ether diamines, polyoxypropylene diamines, poly(ethylene oxide capped oxypropylene) ether diamines, triethyleneglycoldiamines, propylene oxide-based triamines, trimethylolpropane-based triamines, glycerin-based triamines, and mixtures thereof.

The diisocyanate and polyol or polyamine components may be combined to form a prepolymer prior to reaction with a chain extender or curing agent. Any such prepolymer combination is suitable for use in the present invention.

One preferred prepolymer is a toluene diisocyanate prepolymer with polypropylene glycol. Such polypropylene glycol terminated toluene diisocyanate prepolymers are available from Uniroyal Chemical Company of Middlebury, Conn., under the trade name ADIPRENE® LFG963A and LFG640D. Most preferred prepolymers are the polytetramethylene ether glycol terminated toluene diisocyanate prepolymers including those available from Uniroyal Chemical Company of Middlebury, Conn., under the trade name ADIPRENE® LF930A, LF950A, LF601D, and LF751D.

In one embodiment, the number of free NCO groups in the urethane or urea prepolymer may be less than about 14 percent. Preferably the urethane or urea prepolymer has from about 3 percent to about 11 percent, more preferably from about 4 to about 9.5 percent, and even more preferably from about 3 percent to about 9 percent, free NCO on an equivalent weight basis. Polyol chain extenders or curing agents may be primary, secondary, or tertiary polyols.

Non-limiting examples of monomers of these polyols include: trimethylolpropane (TMP), ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, propylene glycol, dipropylene glycol, 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, 1,2-pentanediol, 2,3-pentanediol, 2,5-hexanediol, 2,4-hexanediol, 2-ethyl-1,3-hexanediol, cyclohexanediol, and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol.

Diamines and other suitable polyamines may be added to the compositions of the present invention to function as chain extenders or curing agents. These include primary, secondary and tertiary amines having two or more amines as functional groups. Exemplary diamines include aliphatic diamines, such as tetramethylenediamine, pentamethylenediamine, hexamethylenediamine; alicyclic diamines, such as 3,3'-dimethyl-4,4'-diamino-dicyclohexyl methane; or aromatic diamines, such as diethyl-2,4-toluenediamine-4,4"-methylenebis-(3-chloro,2,6-diethyl)-aniline (available from Air Products and Chemicals Inc., of Allentown, Pa., under the trade name LONZACURE®), 3,3'-dichlorobenzidene; 3,3'-dichloro-4,4'-diaminodiphenyl methane (MOCA); N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine, 3,5-dimethylthio-2,4-toluenediamine; 3,5-dimethylthio-2,6-toluenediamine; N,N'-dialkyldiamino diphenyl methane; trimethylene-glycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate, 4,4'-methylene bis-2-chloroaniline, 2,2',3,3'-tetrachloro-4,4'-diamino-phenyl methane, p,p'-methylenedianiline, p-phenylenediamine or 4,4'-diaminodiphenyl; and 2,4,6-tris(dimethylaminomethyl) phenol.

Depending on their chemical structure, curing agents may be slow- or fast-reacting polyamines or polyols. As described in U.S. Pat. Nos. 6,793,864, 6,719,646 and copending U.S. Patent Publication No. 2004/0201133 A1, (the contents of all of which are hereby incorporated herein by reference), slow-reacting polyamines are diamines having amine groups that are sterically and/or electronically hindered by electron withdrawing groups or bulky groups situated proximate to the amine reaction sites. The spacing of the amine reaction sites will also affect the reactivity speed of the polyamines.

Suitable curatives for use in the present invention are selected from the slow-reacting polyamine group include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine; 3,5-dimethylthio-2,6-toluenediamine; N,N'-dialkyldiamino diphenyl methane; trimethylene-glycol-di-p-aminobenzoate; polytetramethyleneoxide-di-p-aminobenzoate, and mixtures thereof. Of these, 3,5-dimethylthio-2,4-toluenediamine and 3,5-dimethylthio-2,6-toluenediamine are isomers and are sold under the trade name ETHACURE® 300 by Ethyl Corporation. Trimethylene glycol-di-p-aminobenzoate is sold under the trade name POLACURE 740M and polytetramethyleneoxide-di-p-aminobenzoates are sold under the trade name POLAMINES by Polaroid Corporation. N,N'-dialkyldiamino diphenyl methane is sold under the trade name UNILINK® by UOP.

Also included as a curing agent for use in the polyurethane or polyurea compositions used in the present invention are the family of dicyandiamides as described in copending application Ser. No. 11/809,432 filed on May 31, 2007 by Kim et al., the entire contents of which are hereby incorporated by reference

When slow-reacting polyamines are used as the curing agent to produce urethane elastomers, a catalyst is typically needed to promote the reaction between the urethane prepolymer and the curing agent. Specific suitable catalysts include TEDA (1) dissolved in di-propylene glycol (such as TEDA L33 available from Witco Corp. Greenwich, Conn., and DABCO 33 LV available from Air Products and Chemicals Inc.). Catalysts are added at suitable effective amounts, such as from about 2% to about 5%, and (2) more preferably TEDA dissolved in 1,4-butane diol from about 2% to about 5%. Another suitable catalyst includes a blend of 0.5% 33LV or TEDA L33 (above) with 0.1% dibutyl tin dilaurate (available from Witco Corp. or Air Products and Chemicals, Inc.) which is added to a curative such as VIBRACURE® A250. Unfortunately, as is well known in the art, the use of a catalyst can have a significant effect on the ability to control the reaction and thus, on the overall processability.

To eliminate the need for a catalyst, a fast-reacting curing agent, or agents, can be used that does not have electron withdrawing groups or bulky groups that interfere with the reaction groups. However, the problem with lack of control associated with the use of catalysts is not completely eliminated since fast-reacting curing agents also are relatively difficult to control.

Preferred curing agent blends include using dicyandiamide in combination with fast curing agents such as diethyl-2,4-toluenediamine, 4,4"-methylenebis-(3-chloro,2,6-diethyl)-aniline (available from Air Products and Chemicals Inc., of Allentown, Pa., under the trade name LONZACURE®), 3,3'-dichlorobenzidene; 3,3'-dichloro-4,4'-diaminodiphenyl methane (MOCA); N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine and Curalon L, a trade name for a mixture of aromatic diamines sold by Uniroyal, Inc. or any and all combinations thereof. A preferred fast-reacting curing agent is diethyl-2,4-toluene diamine, which has two commercial grades names, Ethacure® 100 and Ethacure® 100LC commercial grade has lower color and less by-product. In other words, it is considered a cleaner product to those skilled in the art.

Advantageously, the use of the Ethacure® 100LC commercial grade results in a golf ball that is less susceptible to yellowing when exposed to UV light conditions. A player appreciates this desirable aesthetic effect although it should be noted that the instant invention may use either of these two commercial grades for the curing agent diethyl-2,4-toluenediamine.

If a reduced-yellowing post curable composition is required the chain extender or curing agent can further comprise a peroxide or peroxide mixture. Before the composition is exposed to sufficient thermal energy to reach the activation temperature of the peroxide, the composition of (a) and (b) behaves as a thermoplastic material. Therefore, it can readily be formed into golf ball layers using injection molding. However, when sufficient thermal energy is applied to bring the composition above the peroxide activation temperature, crosslinking occurs, and the thermoplastic polyurethane is converted into crosslinked polyurethane.

Examples of suitable peroxides for use in compositions within the scope of the present invention include aliphatic peroxides, aromatic peroxides, cyclic peroxides, or mixtures of these. Primary, secondary, or tertiary peroxides can be used, with tertiary peroxides most preferred. Also, peroxides containing more than one peroxy group can be used, such as 2,5-bis-(tert-butylperoxy)-2,5-dimethyl hexane and 1,4-bis-(tert-butylperoxy-isopropyl)-benzene. Also, peroxides that are either symmetrical or asymmetric can be used, such as tert-butylperbenzoate and tert-butylcumylperoxide. Additionally, peroxides having carboxy groups also can be used. Decomposition of peroxides used in compositions within the scope of the present invention can be brought about by applying thermal energy, shear, reactions with other chemical ingredients, or a combination of these. Homolytically decomposed peroxide, heterolytically decomposed peroxide, or a mixture of those can be used to promote crosslinking reactions in compositions within the scope of this invention. Examples of suitable aliphatic peroxides and aromatic peroxides include diacetylperoxide, di-tert-butylperoxide, dibenzoylperoxide, dicumylperoxide, 2,5-bis-(t-butylperoxy)-2,5-dimethyl hexane, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, 2,5-dimethyl-2,5-di(butylperoxy)-3-hexyne, n-butyl-4,4-bis(t-butylperoxyl) valerate, 1,4-bis-(t-butylperoxyisopropyl)-benzene, t-butyl peroxybenzoate, 1,1-bis-(t-butylperoxy)-3,3,5 tri-methylcyclohexane, and di(2,4-dichloro-benzoyl). Peroxides for use within the scope of this invention may be acquired from Akzo Nobel Polymer Chemicals of Chicago, Ill., Atofina of Philadelphia, Pa. and Akrochem of Akron, Ohio. Further details of this post curable system are disclosed in U.S. Pat. No. 6,924,337, the entire contents of which are hereby incorporated by reference.

The core, cover layer and, optionally, one or more inner cover layers of the golf ball may comprise one or more ionomer resins. One family of such resins was developed in the mid-1960's, by E.I. DuPont de Nemours and Co., and sold under the trademark SURLYN®. Preparation of such ionomers is well known, for example see U.S. Pat. No. 3,264,272. Generally speaking, most commercial ionomers are unimodal and consist of a polymer of a mono-olefin, e.g., an alkene, with an unsaturated mono- or dicarboxylic acids having 3 to 12 carbon atoms. An additional monomer in the form of a mono- or dicarboxylic acid ester may also be incorporated in the formulation as a so-called "softening comonomer." The incorporated carboxylic acid groups are then neutralized by a basic metal ion salt, to form the ionomer. The metal cations of the basic metal ion salt used for neutralization include Li^+, Na^+, K^+, Zn^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, and Mg^{2+}, with the Li^+, Na^+, Ca^{2+}, Zn^{2+}, and Mg^{2+} being preferred. The basic metal ion salts include those of for example formic acid, acetic acid, nitric acid, and carbonic acid, hydrogen carbonate salts, oxides, hydroxides, and alkoxides.

The first commercially available ionomer resins contained up to 16 weight percent acrylic or methacrylic acid, although it was also well known at that time that, as a general rule, the hardness of these cover materials could be increased with increasing acid content. Hence, in Research Disclosure 29703, published in January 1989, DuPont disclosed ionomers based on ethylene/acrylic acid or ethylene/methacrylic acid containing acid contents of greater than 15 weight percent. In this same disclosure, DuPont also taught that such so called "high acid ionomers" had significantly improved stiffness and hardness and thus could be advantageously used in golf ball construction, when used either singly or in a blend with other ionomers.

More recently, high acid ionomers can be ionomer resins with acrylic or methacrylic acid units present from 16 wt. % to about 35 wt. % in the polymer. Generally, such a high acid ionomer will have a flexural modulus from about 50,000 psi to about 125,000 psi.

Ionomer resins further comprising a softening comonomer, present from about 10 wt. % to about 50 wt. % in the polymer, have a flexural modulus from about 2,000 psi to about 10,000 psi, and are sometimes referred to as "soft" or "very low modulus" ionomers. Typical softening comonomers include n-butyl acrylate, iso-butyl acrylate, n-butyl methacrylate, methyl acrylate and methyl methacrylate.

Today, there are a wide variety of commercially available ionomer resins based both on copolymers of ethylene and (meth)acrylic acid or terpolymers of ethylene and (meth) acrylic acid and (meth)acrylate, all of which can be used as a golf ball component. The properties of these ionomer resins can vary widely due to variations in acid content, softening comonomer content, the degree of neutralization, and the type of metal ion used in the neutralization. The full range commercially available typically includes ionomers of polymers of general formula, E/X/Y polymer, wherein E is ethylene, X is a C_3 to C_8 α,β ethylenically unsaturated carboxylic acid, such as acrylic or methacrylic acid, and is present in an amount from about 0 wt. % to about 50 wt. %, particularly about 2 to about 30 weight %, of the E/X/Y copolymer, and Y is a softening comonomer selected from the group consisting of alkyl acrylate and alkyl methacrylate, such as methyl acrylate or methyl methacrylate, and wherein the alkyl groups have from 1-8 carbon atoms, Y is in the range of 0 to about 50 weight %, particularly about 5 wt. % to about 35 wt. %, of the E/X/Y copolymer, and wherein the acid groups present in said ionomeric polymer are partially (e.g., about 1% to about 90%) neutralized with a metal selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc or aluminum, or a combination of such cations.

The ionomer may also be a so-called bimodal ionomer as described in U.S. Pat. No. 6,562,906 (the entire contents of which are herein incorporated by reference). These ionomers are bimodal as they are prepared from blends comprising polymers of different molecular weights. Specifically they include bimodal polymer blend compositions comprising:

a) a high molecular weight component having weight average molecular weight (M_w) of about 80,000 to about 500,000 and comprising one or more ethylene/α,β-ethylenically unsaturated C_{3-8} carboxylic acid copolymers and/or one or more ethylene, alkyl (meth)acrylate, (meth)acrylic acid terpolymers; said high molecular weight component being partially neutralized with metal ions selected from the group consisting of lithium, sodium, zinc, calcium, magnesium, and a mixture of any these; and

b) a low molecular weight component having a weight average molecular weight (M_w) of about from about 2,000 to about 30,000 and comprising one or more ethylene/α,β-ethylenically unsaturated C_{3-8} carboxylic acid copolymers and/or one or more ethylene, alkyl (meth)acrylate, (meth)acrylic acid terpolymers; said low molecular weight component being partially neutralized with metal ions selected from the group consisting of lithium, sodium, zinc, calcium, magnesium, and a mixture of any these.

In addition to the unimodal and bimodal ionomers, also included are the so-called "modified ionomers" examples of which are described in U.S. Pat. Nos. 6,100,321, 6,329,458 and 6,616,552 and U.S. Patent Publication No. US 2003/0158312 A1, the entire contents of all of which are herein incorporated by reference.

The modified unimodal ionomers may be prepared by mixing:

a) an ionomeric polymer comprising ethylene, from 5 to 25 weight percent (meth)acrylic acid, and from 0 to 40 weight percent of a (meth)acrylate monomer, said ionomeric polymer neutralized with metal ions selected from the group consisting of lithium, sodium, zinc, calcium, magnesium, and a mixture of any of these; and

b) from about 5 to about 40 weight percent (based on the total weight of said modified ionomeric polymer) of one or more fatty acids or metal salts of said fatty acid, the metal selected from the group consisting of calcium, sodium, zinc, potassium, and lithium, barium and magnesium and the fatty acid preferably being stearic acid.

The modified bimodal ionomers, which are ionomers derived from the earlier described bimodal ethylene/carboxylic acid polymers (as described in U.S. Pat. No. 6,562,906, the entire contents of which are herein incorporated by reference), are prepared by mixing;

a) a high molecular weight component having weight average molecular weight (M_w) of about 80,000 to about 500,000 and comprising one or more ethylene/α,β-ethylenically unsaturated C_{3-8} carboxylic acid copolymers and/or one or more ethylene, alkyl (meth)acrylate, (meth)acrylic acid terpolymers; said high molecular weight component being partially neutralized with metal ions selected from the group consisting of lithium, sodium, zinc, calcium, potassium, magnesium, and a mixture of any of these; and

b) a low molecular weight component having a weight average molecular weight (M_w) of about from about 2,000 to about 30,000 and comprising one or more ethylene/α,β-ethylenically unsaturated C_{3-8} carboxylic acid copolymers and/or one or more ethylene, alkyl (meth)acrylate, (meth)acrylic acid terpolymers; said low molecular weight component being partially neutralized with metal ions selected from the group consisting of lithium, sodium, zinc, calcium, potassium, magnesium, and a mixture of any of these; and

c) from about 5 to about 40 weight percent (based on the total weight of said modified ionomeric polymer) of one or more fatty acids or metal salts of said fatty acid, the metal selected from the group consisting of calcium, sodium, zinc, potassium and lithium, barium and magnesium and the fatty acid preferably being stearic acid.

The fatty or waxy acid salts utilized in the various modified ionomers are composed of a chain of alkyl groups containing from about 4 to 75 carbon atoms (usually even numbered) and characterized by a —COOH terminal group. The generic formula for all fatty and waxy acids above acetic acid is $CH_3(CH_2)_XCOOH$, wherein the carbon atom count includes the carboxyl group. The fatty or waxy acids utilized to produce the fatty or waxy acid salts modifiers may be saturated or unsaturated, and they may be present in solid, semi-solid or liquid form.

Examples of suitable saturated fatty acids, i.e., fatty acids in which the carbon atoms of the alkyl chain are connected by single bonds, include but are not limited to stearic acid (C_{18}, i.e., $CH_3(CH_2)_{16}COOH$), palmitic acid (C_{16}, i.e., $CH_3(CH_2)_{14}COOH$), pelargonic acid (C_9, i.e., $CH_3(CH_2)_7COOH$) and lauric acid (C_{12}, i.e., $CH_3(CH_2)_{10}OCOOH$). Examples of suitable unsaturated fatty acids, i.e., a fatty acid in which there are one or more double bonds between the carbon atoms in the alkyl chain, include but are not limited to oleic acid (C_{13}, i.e., $CH_3(CH_2)_7CH{:}CH(CH_2)_7COOH$).

The source of the metal ions used to produce the metal salts of the fatty or waxy acid salts used in the various modified ionomers are generally various metal salts which provide the metal ions capable of neutralizing, to various extents, the carboxylic acid groups of the fatty acids. These include the sulfate, carbonate, acetate and hydroxylate salts of zinc, barium, calcium and magnesium.

Since the fatty acid salts modifiers comprise various combinations of fatty acids neutralized with a large number of different metal ions, several different types of fatty acid salts may be utilized in the invention, including metal stearates, laureates, oleates, and palmitates, with calcium, zinc, sodium, lithium, potassium and magnesium stearate being preferred, and calcium and sodium stearate being most preferred.

The fatty or waxy acid or metal salt of said fatty or waxy acid is present in the modified ionomeric polymers in an amount of from about 5 to about 40, preferably from about 7 to about 35, more preferably from about 8 to about 20 weight percent (based on the total weight of said modified ionomeric polymer).

As a result of the addition of the one or more metal salts of a fatty or waxy acid, from about 40 to 100, preferably from about 50 to 100, more preferably from about 70 to 100 percent of the acidic groups in the final modified ionomeric polymer composition are neutralized by a metal ion.

An example of such a modified ionomer polymer is DuPont® HPF-1000 available from E. I. DuPont de Nemours and Co. Inc.

In yet another embodiment, a blend of an ionomer and a block copolymer can be included in the composition. An example of a block copolymer is a styrenic block copolymer, the block copolymer incorporating a first polymer block having an aromatic vinyl compound, a second polymer block having a conjugated diene compound, and optionally a hydroxyl group located at a block copolymer, or the hydrogenation product of the block copolymer, in which the ratio of block copolymer to ionomer ranges from 5:95 to 95:5 by weight, more preferably from about 10:90 to about 90:10 by weight, more preferably from about 20:80 to about 80:20 by weight, more preferably from about 30:70 to about 70:30 by weight and most preferably from about 35:65 to about 65:35 by weight. A preferred block copolymer is SEPTON HG-252. Such blends are described in more detail in commonly-assigned U.S. Pat. No. 6,861,474 and U.S. Patent Publication No. 2003/0224871 both of which are incorporated herein by reference in their entireties.

In a further embodiment, the core, mantle and/or cover layers (and particularly a mantle layer) can comprise a composition prepared by blending together at least three materials, identified as Components A, B, and C, and melt-processing these components to form in-situ a polymer blend composition incorporating a pseudo-crosslinked polymer network. Such blends are described in more detail in commonly-assigned U.S. Pat. No. 6,930,150, which is incorporated by reference herein in its entirety. Component A is a monomer, oligomer, prepolymer or polymer that incorporates at least five percent by weight of at least one type of an anionic functional group, and more preferably between about 5% and 50% by weight. Component B is a monomer, oligomer, or polymer that incorporates less by weight of anionic functional groups than does Component A, Component B preferably incorporates less than about 25% by weight of anionic functional groups, more preferably less than about 20% by weight, more preferably less than about 10% by weight, and most preferably Component B is free of anionic functional groups. Component C incorporates a metal cation, preferably as a metal salt. The pseudo-crosslinked network structure is formed in-situ, not by covalent bonds, but instead by ionic clustering of the reacted functional groups of Component A. The method can incorporate blending together more than one of any of Components A, B, or C.

The polymer blend can include either Component A or B dispersed in a phase of the other. Preferably, blend compositions comprises between about 1% and about 99% by weight of Component A based on the combined weight of Components A and B, more preferably between about 10% and about 90%, more preferably between about 20% and about 80%, and most preferably, between about 30% and about 70%. Component C is present in a quantity sufficient to produce the preferred amount of reaction of the anionic functional groups of Component A after sufficient melt-processing. Preferably, after melt-processing at least about 5% of the anionic functional groups in the chemical structure of Component A have been consumed, more preferably between about 10% and about 90%, more preferably between about 10% and about 80%, and most preferably between about 10% and about 70%.

The composition preferably is prepared by mixing the above materials into each other thoroughly, either by using a dispersive mixing mechanism, a distributive mixing mechanism, or a combination of these. These mixing methods are well known in the manufacture of polymer blends. As a result of this mixing, the anionic functional group of Component A is dispersed evenly throughout the mixture. Next, reaction is made to take place in-situ at the site of the anionic functional groups of Component A with Component C in the presence of Component B. This reaction is prompted by addition of heat to the mixture. The reaction results in the formation of ionic clusters in Component A and formation of a pseudo-crosslinked structure of Component A in the presence of Component B. Depending upon the structure of Component B, this pseudo-crosslinked Component A can combine with Component B to form a variety of interpenetrating network structures. For example, the materials can form a pseudo-crosslinked network of Component A dispersed in the phase of Component B, or Component B can be dispersed in the phase of the pseudo-crosslinked network of Component A. Component B may or may not also form a network, depending upon its structure, resulting in either: a fully-interpenetrating network, i.e., two independent networks of Components A and B penetrating each other, but not covalently bonded to each other; or, a semi-interpenetrating network of Components A and B, in which Component B forms a linear, grafted, or branched polymer interspersed in the network of Component A. For example, a reactive functional group or an unsaturation in Component B can be reacted to form a crosslinked structure in the presence of the in-situ-formed, pseudo-crosslinked structure of Component A, leading to formation of a fully-interpenetrating network. Any anionic functional groups in Component B also can be reacted with the metal cation of Component C, resulting in pseudo-crosslinking via ionic cluster attraction of Component A to Component B.

The level of in-situ-formed pseudo-crosslinking in the compositions formed by the present methods can be controlled as desired by selection and ratio of Components A and B, amount and type of anionic functional group, amount and type of metal cation in Component C, type and degree of chemical reaction in Component B, and degree of pseudo-crosslinking produced of Components A and B.

As discussed above, the mechanical and thermal properties of the polymer blend for the inner mantle layer and/or the outer mantle layer can be controlled as required by a modifying any of a number of factors, including: chemical structure of Components A and B, particularly the amount and type of anionic functional groups; mean molecular weight and molecular weight distribution of Components A and B; linearity and crystallinity of Components A and B; type of metal cation in Component C; degree of reaction achieved between the anionic functional groups and the metal cation; mix ratio of Component A to Component B; type and degree of chemical reaction in Component B; presence of chemical reaction, such as a crosslinking reaction, between Components A and B; and the particular mixing methods and conditions used.

As discussed above, Component A can be any monomer, oligomer, prepolymer, or polymer incorporating at least 5% by weight of anionic functional groups. Those anionic functional groups can be incorporated into monomeric, oligomeric, prepolymeric, or polymeric structures during the synthesis of Component A, or they can be incorporated into a pre-existing monomer, oligomer, prepolymer, or polymer through sulfonation, phosphonation, or carboxylation to produce Component A.

Preferred, but non-limiting, examples of suitable copolymers and terpolymers include copolymers or terpolymers of: ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/itaconic acid, ethylene/methyl hydrogen maleate, ethylene/maleic acid, ethylene/methacrylic acid/ethylacrylate, ethylene/itaconic acid/methyl methacrylate, ethylene/methyl hydrogen maleate/ethyl acrylate, ethylene/methacrylic acid/vinyl acetate, ethylene/acrylic acid/vinyl alcohol, ethylene/propylene/acrylic acid, ethylene/styrene/acrylic acid, ethylene/methacrylic acid/acrylonitrile, ethylene/fumaric acid/vinyl methyl ether, ethylene/vinyl chloride/acrylic acid, ethylene/vinyldiene chloride/acrylic acid, ethylene/vinyl fluoride/methacrylic acid, and ethylene/chlorotrifluoroethylene/methacrylic acid, or any metallocene-catalyzed polymers of the above-listed species.

Preferred examples of Component A are polymers of i) ethylene and/or an alpha olefin; and ii) an α,β-ethylenically unsaturated C_3-C_{20} carboxylic acid or anhydride, or an α,β-ethylenically unsaturated C_3-C_{20} sulfonic acid or anhydride or an α,β-ethylenically unsaturated C_3-C_{20} phosphoric acid or anhydride and, optionally iii) a C_1-C_{10} ester of an α,β-ethylenically unsaturated C_3-C_{20} carboxylic acid or a C_1-C_{10} ester of an α,β-ethylenically unsaturated C_3-C_{20} sulfonic acid or a C_1-C_{10} ester of an α,β-ethylenically unsaturated C_3-C_{20} phosphoric acid.

Preferably, the alpha-olefin has from 2 to 10 carbon atoms and is preferably ethylene, and the unsaturated carboxylic acid is a carboxylic acid having from about 3 to 8 carbons. Examples of such acids include acrylic acid, methacrylic acid, ethacrylic acid, chloroacrylic acid, crotonic acid, maleic acid, fumaric acid, and itaconic acid, with acrylic acid being preferred. Preferably, the carboxylic acid ester if present may be selected from the group consisting of vinyl esters of aliphatic carboxylic acids wherein the acids have 2 to 10 carbon atoms and vinyl ethers wherein the alkyl groups contain 1 to 10 carbon atoms.

The acid content of the polymer may contain anywhere from 1 to 30 percent by weight acid. In some instances, it is preferable to utilize a high acid copolymer (i.e., a copolymer containing greater than 16% by weight acid, preferably from about 17 to about 25 weight percent acid, and more preferably about 20 weight percent acid).

Examples of such polymers suitable for use include, but are not limited to, an ethylene/acrylic acid copolymer, an ethylene/methacrylic acid copolymer, an ethylene/itaconic acid copolymer, an ethylene/maleic acid copolymer, an ethylene/methacrylic acid/vinyl acetate copolymer, an ethylene/acrylic acid/vinyl alcohol copolymer, and the like.

Most preferred are ethylene/(meth)acrylic acid copolymers and ethylene/(meth)acrylic acid/alkyl (meth)acrylate terpolymers, or ethylene and/or propylene maleic anhydride copolymers and terpolymers.

Examples of such polymers which are commercially available include, but are not limited to, the Escor® 5000, 5001, 5020, 5050, 5070, 5100, 5110 and 5200 series of ethylene-acrylic acid copolymers sold by Exxon and the PRIMACOR® 1321, 1410, 1410-XT, 1420, 1430, 2912, 3150, 3330, 3340, 3440, 3460, 4311, 4608 and 5980 series of ethylene-acrylic acid copolymers sold by The Dow Chemical Company, Midland, Mich.

Also included are the bimodal ethylene/carboxylic acid polymers as described in U.S. Pat. No. 6,562,906. These polymers comprise ethylene/α,β-ethylenically unsaturated C_{3-8} carboxylic acid high copolymers, particularly ethylene (meth)acrylic acid copolymers and ethylene, alkyl (meth) acrylate, (meth)acrylic acid terpolymers, having molecular weights of about 80,000 to about 500,000 which are melt blended with ethylene/α,β-ethylenically unsaturated C_{3-8} carboxylic acid copolymers, particularly ethylene/(meth) acrylic acid copolymers having weight average molecular weights of about 2,000 to about 30,000.

As discussed above, Component B can be any monomer, oligomer, or polymer, preferably having a lower weight percentage of anionic functional groups than that present in Component A in the weight ranges discussed above, and most preferably free of such functional groups. Examples of suitable materials for Component B include, but are not limited to, the following: thermoplastic elastomer, thermoset elastomer, synthetic rubber, thermoplastic vulcanizate, copolymeric ionomer, terpolymeric ionomer, polycarbonate, polyolefin, polyamide, copolymeric polyamide, polyesters, polyvinyl alcohols, acrylonitrile-butadiene-styrene copolymers, polyurethane, polyarylate, polyacrylate, polyphenyl ether, modified-polyphenyl ether, high-impact polystyrene, diallyl phthalate polymer, metallocene catalyzed polymers, acrylonitrile-styrene-butadiene (ABS), styrene-acrylonitrile (SAN) (including olefin-modified SAN and acrilonitrile styrene acrylonitrile), styrene-maleic anhydryde (S/MA) polymer, styrenic copolymer, functionalized styrenic copolymer, functionalized styrenic terpolymer, styrenic terpolymer, cellulose polymer, liquid crystal polymer (LCP), ethylene-propylene-diene terpolymer (EPDM), ethylene-propylene copolymer, ethylene vinyl acetate, polyurea, and polysiloxane or any metallocene-catalyzed polymers of these species. Particularly suitable polymers for use as Component B include polyethylene-terephthalate, polybutyleneterephthalate, polytrimethylene-terephthalate, ethylene-carbon monoxide copolymer, polyvinyl-diene fluorides, polyphenylenesulfide, polypropyleneoxide, polyphenyloxide, polypropylene, functionalized polypropylene, polyethylene, ethylene-octene copolymer, ethylene-methyl acrylate, ethylene-butyl acrylate, polycarbonate, polysiloxane, functionalized polysiloxane, copolymeric ionomer, terpolymeric ionomer, polyetherester elastomer, polyesterester elastomer, polyetheramide elastomer, propylene-butadiene copolymer, modified copolymer of ethylene and propylene, styrenic copolymer (including styrenic block copolymer and randomly distributed styrenic copolymer, such as styrene-isobutylene copolymer and styrene-butadiene copolymer), partially or fully hydrogenated styrene-butadiene-styrene block copolymers such as styrene-(ethylene-propylene)-styrene or styrene-(ethylene-butylene)-styrene block copolymers, partially or fully hydrogenated styrene-butadiene-styrene block copolymers with functional group, polymers based on ethylene-propylene-(diene), polymers based on functionalized ethylene-propylene-diene), dynamically vulcanized polypropylene/ethylene-propylene-diene-copolymer, thermoplastic vulcanizates based on ethylene-propylene-(diene), thermoplastic polyetherurethane, thermoplastic polyesterurethane, compositions for making thermoset polyurethane, thermoset polyurethane, natural rubber, styrene-butadiene rubber, nitrile rubber, chloroprene rubber, fluorocarbon rubber, butyl rubber, acrylic rubber, silicone rubber, chlorosulfonated polyethylene, polyisobutylene, alfin rubber, polyester rubber, epichlorohydrin rubber, chlorinated isobutylene-isoprene rubber, nitrile-isobutylene rubber, 1,2-polybutadiene, 1,4-polybutadiene, cis-polyisoprene, trans-polyisoprene, and polybutylene-octene.

Preferred materials for use as Component B include polyester elastomers marketed under the name PEBAX and LOTADER marketed by ATOFINA Chemicals of Philadelphia, Pa.; HYTREL, FUSABOND, and NUCREL marketed by E.I. DuPont de Nemours & Co. of Wilmington, Del.; SKYPEL and SKYTHANE by S.K. Chemicals of Seoul, South Korea; SEPTON and HYBRAR marketed by Kuraray Company of Kurashiki, Japan; ESTHANE by Noveon; and KRATON marketed by Kraton Polymers. A most preferred material for use as Component B is SEPTON HG-252.

As stated above, Component C is a metal cation. These metals are from groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIIA, VIIB, VIIIB and VIJIB of the periodic table. Examples of these metals include lithium, sodium, magnesium, aluminum, potassium, calcium, manganese, tungsten, titanium, iron, cobalt, nickel, hafnium, copper, zinc, barium, zirconium, and tin. Suitable metal compounds for use as a source of Component C are, for example, metal salts, preferably metal hydroxides, metal carbonates, or metal acetates. In addition to Components A, B, and C, other materials commonly used in polymer blend compositions, can be incorporated into compositions prepared using these methods, including: crosslinking agents, co-crosslinking agents, accelerators, activators, UV-active chemicals such as UV initiators, EB-active chemicals, colorants, UV stabilizers, optical brighteners, antioxidants, processing aids, mold release agents, foaming agents, and organic, inorganic or metallic fillers or fibers, including fillers to adjust specific gravity.

Various known methods are suitable for preparation of polymer blends. For example, the three components can be premixed together in any type of suitable mixer, such as a V-blender, tumbler mixer, or blade mixer. This premix then can be melt-processed using an internal mixer, such as Banbury mixer, roll-mill or combination of these, to produce a reaction product of the anionic functional groups of Component A by Component C in the presence of Component B. Alternatively, the premix can be melt-processed using an extruder, such as single screw, co-rotating twin screw, or counter-rotating twin screw extruder, to produce the reaction product. The mixing methods discussed above can be used together to melt-mix the three components to prepare the compositions of the present invention. Also, the components can be fed into an extruder simultaneously or sequentially.

Most preferably, Components A and B are melt-mixed together without Component C, with or without the premixing discussed above, to produce a melt-mixture of the two components. Then, Component C separately is mixed into the blend of Components A and B. This mixture is melt-mixed to produce the reaction product. This two-step mixing can be performed in a single process, such as, for example, an extrusion process using a proper barrel length or screw configuration, along with a multiple feeding system. In this case, Components A and B can be fed into the extruder through a main hopper to be melted and well-mixed while flowing downstream through the extruder. Then Component C can be fed into the extruder to react with the mixture of Components A and B between the feeding port for Component C and the die head of the extruder. The final polymer composition then exits from the die. If desired, any extra steps of melt-mixing can be added to either approach of the method of the present invention to provide for improved mixing or completion of the reaction between Components A and C. Also, additional components discussed above can be incorporated either into a premix, or at any of the melt-mixing stages. Alternatively, Components A, B, and C can be melt-mixed simultaneously to form in-situ a pseudo-crosslinked structure of Component A in the presence of Component B, either as a fully or semi-interpenetrating network.

Illustrative polyamides for use in the golf balls of the present invention include those obtained by: (1) polycondensation of (a) a dicarboxylic acid, such as oxalic acid, adipic acid, sebacic acid, terephthalic acid, isophthalic acid, or 1,4-cyclohexanedicarboxylic acid, with (b) a diamine, such as ethylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, decamethylenediamine, 1,4-cyclohexyldiamine or m-xylylenediamine; (2) a ring-opening polymerization of cyclic lactam, such as c-caprolactam or ω-laurolactam; (3) polycondensation of an aminocarboxylic acid, such as 6-aminocaproic acid, 9-aminononanoic acid, 11-aminoundecanoic acid or 12-aminododecanoic acid; (4) copolymerization of a cyclic lactam with a dicarboxylic acid and a diamine; or any combination of (1)-(4). In certain examples, the dicarboxylic acid may be an aromatic dicarboxylic acid or a cycloaliphatic dicarboxylic acid. In certain examples, the diamine may be an aromatic diamine or a cycloaliphatic diamine. Specific examples of suitable polyamides include polyamide 6; polyamide 11; polyamide 12; polyamide 4,6; polyamide 6,6; polyamide 6,9; polyamide 6,10; polyamide 6,12; polyamide MXD6; PA12,CX; PA 12, IT; PPA; PA6, IT; and PA6/PPE.

The polyamide may be any homopolyamide or copolyamide. One example of a group of suitable polyamides is thermoplastic polyamide elastomers. Thermoplastic polyamide elastomers typically are copolymers of a polyamide and polyester or polyether. For example, the thermoplastic polyamide elastomer can contain a polyamide (Nylon 6, Nylon 66, Nylon 11, Nylon 12 and the like) as a hard segment and a polyether or polyester as a soft segment. In one specific example, the thermoplastic polyamides are amorphous copolyamides based on polyamide (PA 12).

One class of copolyamide elastomers are polyether amide elastomers. Illustrative examples of polyether amide elastomers are those that result from the copolycondensation of polyamide blocks having reactive chain ends with polyether blocks having reactive chain ends, including:

(1) polyamide blocks of diamine chain ends with polyoxyalkylene sequences of dicarboxylic chains;

(2) polyamide blocks of dicarboxylic chain ends with polyoxyalkylene sequences of diamine chain ends obtained by cyanoethylation and hydrogenation of polyoxyalkylene alpha-omega dihydroxylated aliphatic sequences known as polyether diols; and

(3) polyamide blocks of dicarboxylic chain ends with polyether diols, the products obtained, in this particular case, being polyetheresteramides.

More specifically, the polyamide elastomer can be prepared by polycondensation of the components (i) a diamine and a dicarboxylate, lactames or an amino dicarboxylic acid (PA component), (ii) a polyoxyalkylene glycol such as polyoxyethylene glycol, polyoxy propylene glycol (PG component) and (iii) a dicarboxylic acid.

The polyamide blocks of dicarboxylic chain ends come, for example, from the condensation of alpha-omega aminocarboxylic acids of lactam or of carboxylic diacids and diamines in the presence of a carboxylic diacid which limits the chain length. The molecular weight of the polyamide sequences is preferably between about 300 and 15,000, and more preferably between about 600 and 5,000. The molecular weight of the polyether sequences is preferably between about 100 and 6,000, and more preferably between about 200 and 3,000.

The amide block polyethers may also comprise randomly distributed units. These polymers may be prepared by the simultaneous reaction of polyether and precursor of polyamide blocks. For example, the polyether diol may react with a lactam (or alpha-omega amino acid) and a diacid which limits the chain in the presence of water. A polymer is obtained that has primarily polyether blocks and/or polyamide blocks of very variable length, but also the various reactive groups that have reacted in a random manner and which are distributed statistically along the polymer chain.

Suitable amide block polyethers include those as disclosed in U.S. Pat. Nos. 4,331,786; 4,115,475; 4,195,015; 4,839,441; 4,864,014; 4,230,848 and 4,332,920.

The polyether may be, for example, a polyethylene glycol (PEG), a polypropylene glycol (PPG), or a polytetramethylene glycol (PTMG), also designated as polytetrahydrofurane (PTHF). The polyether blocks may be along the polymer chain in the form of diols or diamines. However, for reasons of simplification, they are designated PEG blocks, or PPG blocks, or also PTMG blocks.

The polyether block comprises different units such as units which derive from ethylene glycol, propylene glycol, or tetramethylene glycol.

The amide block polyether comprises at least one type of polyamide block and one type of polyether block. Mixing of two or more polymers with polyamide blocks and polyether blocks may also be used. The amide block polyether also can comprise any amide structure made from the method described on the above.

Preferably, the amide block polyether is such that it represents the major component in weight, i.e., that the amount of polyamide which is under the block configuration and that which is eventually distributed statistically in the chain represents 50 weight percent or more of the amide block polyether. Advantageously, the amount of polyamide and the amount of polyether is in a ratio (polyamide/polyether) of 1/1 to 3/1.

One type of polyetherester elastomer is the family of Pebax, which are available from Elf-Atochem Company. Preferably, the choice can be made from among Pebax 2533, 3533, 4033, 1205, 7033 and 7233. Blends or combinations of Pebax 2533, 3533, 4033, 1205, 7033 and 7233 can also be prepared, as well. Pebax 2533 has a hardness of about 25 shore D (according to ASTM D-2240), a Flexural Modulus of 2.1 kpsi (according to ASTM D-790), and a Bayshore resilience of about 62% (according to ASTM D-2632). Pebax 3533 has a hardness of about 35 shore D (according to ASTM D-2240), a Flexural Modulus of 2.8 kpsi (according to ASTM D-790), and a Bayshore resilience of about 59% (according to ASTM D-2632). Pebax 7033 has a hardness of about 69 shore D (according to ASTM D-2240) and a Flexural Modulus of 67 kpsi (according to ASTM D-790). Pebax 7333 has a hardness of about 72 shore D (according to ASTM D-2240) and a Flexural Modulus of 107 kpsi (according to ASTM D-790).

Some examples of suitable polyamides for use include those commercially available under the tradenames PEBAX, CRISTAMID and RILSAN marketed by Atofina Chemicals of Philadelphia, Pa., GRIVORY and GRILAMID marketed by EMS Chemie of Sumter, S.C., TROGAMID and VESTAMID available from Degussa, and ZYTEL marketed by E.I. DuPont de Nemours & Co., of Wilmington, Del.

The core, mantle and cover compositions can also incorporate one or more fillers. Such fillers are typically in a finely divided form, for example, in a size generally less than about 20 mesh, preferably less than about 100 mesh U.S. standard size, except for fibers and flock, which are generally elongated. Flock and fiber sizes should be small enough to facilitate processing. Filler particle size will depend upon desired effect, cost, ease of addition, and dusting considerations. The appropriate amounts of filler required will vary depending on the application but typically can be readily determined without undue experimentation.

The filler preferably is selected from the group consisting of precipitated hydrated silica, limestone, clay, talc, asbestos, barytes, glass fibers, aramid fibers, mica, calcium metasilicate, barium sulfate, zinc sulfide, lithopone, silicates, silicon carbide, diatomaceous earth, carbonates such as calcium or magnesium or barium carbonate, sulfates such as calcium or magnesium or barium sulfate, metals, including tungsten steel copper, cobalt or iron, metal alloys, tungsten carbide, metal oxides, metal stearates, and other particulate carbonaceous materials, and any and all, combinations thereof. Preferred examples of fillers include metal oxides, such as zinc oxide and magnesium oxide. In another preferred embodiment the filler comprises a continuous or non-continuous fiber. In another preferred embodiment the filler comprises one or more so called nanofillers, as described in U.S. Pat. No. 6,794,447 and U.S. Patent Publication No. 2004-0092336A1 published May 13, 2004 and U.S. Patent Publication No. 2005-0059756A1 published Mar. 17, 2005, the entire contents of each of which are herein incorporated by reference.

Inorganic nanofiller material generally is made of clay, such as hydrotalcite, phyllosilicate, saponite, hectorite, beidellite, stevensite, vermiculite, halloysite, mica, montmorillonite, micafluoride, or octosilicate. To facilitate incorporation of the nanofiller material into a polymer material, either in preparing nanocomposite materials or in preparing polymer-based golf ball compositions, the clay particles generally are coated or treated by a suitable compatibilizing agent. The compatibilizing agent allows for superior linkage between the inorganic and organic material, and it also can account for the hydrophilic nature of the inorganic nanofiller material and the possibly hydrophobic nature of the polymer. Compatibilizing agents may exhibit a variety of different structures depending upon the nature of both the inorganic nanofiller material and the target matrix polymer. Non-limiting examples include hydroxy-, thiol-, amino-, epoxy-, carboxylic acid-, ester-, amide-, and siloxy-group containing compounds, oligomers or polymers. The nanofiller materials can be incorporated into the polymer either by dispersion into the particular monomer or oligomer prior to polymerization, or by melt compounding of the particles into the matrix polymer. Examples of commercial nanofillers are various Cloisite grades including 10A, 15A, 20A, 25A, 30B, and NA+ of Southern Clay Products (Gonzales, Tex.) and the Nanomer grades including 1.24TL and C.30EVA of Nanocor, Inc. (Arlington Heights, Ill.).

As mentioned above, the nanofiller particles have an aggregate structure with the aggregates particle sizes in the micron range and above. However, these aggregates have a stacked plate structure with the individual platelets being roughly 1 nanometer (nm) thick and 100 to 1000 nm across. As a result, nanofillers have extremely high surface area, resulting in high reinforcement efficiency to the material at low loading levels of the particles. The sub-micron-sized particles enhance the stiffness of the material, without increasing its weight or opacity and without reducing the material's low-temperature toughness.

Nanofillers when added into a matrix polymer, can be mixed in three ways. In one type of mixing there is dispersion of the aggregate structures within the matrix polymer, but on mixing no interaction of the matrix polymer with the aggregate platelet structure occurs, and thus the stacked platelet structure is essentially maintained. As used herein, this type of mixing is defined as "undispersed".

However, if the nanofiller material is selected correctly, the matrix polymer chains can penetrate into the aggregates and separate the platelets, and thus when viewed by transmission electron microscopy or x-ray diffraction, the aggregates of platelets are expanded. At this point the nanofiller is said to be substantially evenly dispersed within and reacted into the structure of the matrix polymer. This level of expansion can occur to differing degrees. If small amounts of the matrix polymer are layered between the individual platelets then, as used herein, this type of mixing is known as "intercalation".

In some cases, further penetration of the matrix polymer chains into the aggregate structure separates the platelets, and leads to a complete breaking up of the platelet's stacked structure in the aggregate and thus when viewed by transmission electron microscopy (TEM), the individual platelets are thoroughly mixed throughout the matrix polymer. As used herein, this type of mixing is known as "exfoliated". An exfoliated nanofiller has the platelets fully dispersed throughout the polymer matrix; the platelets may be dispersed unevenly but preferably are dispersed evenly.

While not wishing to be limited to any theory, one possible explanation of the differing degrees of dispersion of such nanofillers within the matrix polymer structure is the effect of the compatibilizer surface coating on the interaction between the nanofiller platelet structure and the matrix polymer. By careful selection of the nanofiller it is possible to vary the penetration of the matrix polymer into the platelet structure of the nanofiller on mixing. Thus, the degree of interaction and intrusion of the polymer matrix into the nanofiller controls the separation and dispersion of the individual platelets of the nanofiller within the polymer matrix. This interaction of the polymer matrix and the platelet structure of the nanofiller is defined herein as the nanofiller "reacting into the structure of the polymer" and the subsequent dispersion of the platelets within the polymer matrix is defined herein as the nanofiller "being substantially evenly dispersed" within the structure of the polymer matrix.

If no compatibilizer is present on the surface of a filler such as a clay, or if the coating of the clay is attempted after its addition to the polymer matrix, then the penetration of the matrix polymer into the nanofiller is much less efficient, very little separation and no dispersion of the individual clay platelets occurs within the matrix polymer.

As used herein, a "nanocomposite" is defined as a polymer matrix having nanofiller intercalated or exfoliated within the matrix. Physical properties of the polymer will change with the addition of nanofiller and the physical properties of the polymer are expected to improve even more as the nanofiller is dispersed into the polymer matrix to form a nanocomposite.

Materials incorporating nanofiller materials can provide these property improvements at much lower densities than those incorporating conventional fillers. For example, a nylon-6 nanocomposite material manufactured by RTP Corporation of Wichita, Kans. uses a 3% to 5% clay loading and has a tensile strength of 11,800 psi and a specific gravity of 1.14, while a conventional 30% mineral-filled material has a tensile strength of 8,000 psi and a specific gravity of 1.36. Because use of nanocomposite materials with lower loadings of inorganic materials than conventional fillers provides the same properties, this use allows products to be lighter than those with conventional fillers, while maintaining those same properties.

Nanocomposite materials are materials incorporating from about 0.1% to about 20%, preferably from about 0.1% to about 15%, and most preferably from about 0.1% to about 10% of nanofiller reacted into and substantially dispersed through intercalation or exfoliation into the structure of an organic material, such as a polymer, to provide strength, temperature resistance, and other property improvements to the resulting composite. Descriptions of particular nanocomposite materials and their manufacture can be found in U.S. Pat. No. 5,962,553 to Ellsworth, U.S. Pat. No. 5,385,776 to Maxfield et al., and U.S. Pat. No. 4,894,411 to Okada et al. Examples of nanocomposite materials currently marketed include M1030D, manufactured by Unitika Limited, of Osaka, Japan, and 1015C2, manufactured by UBE America of New York, N.Y.

When nanocomposites are blended with other polymer systems, the nanocomposite may be considered a type of nanofiller concentrate. However, a nanofiller concentrate may be more generally a polymer into which nanofiller is mixed; a nanofiller concentrate does not require that the nanofiller has reacted and/or dispersed evenly into the carrier polymer.

Preferably the nanofiller material is added to the polymeric composition in an amount of from about 0.1% to about 20%, preferably from about 0.1% to about 15%, and most preferably from about 0.1% to about 10% by weight of nanofiller reacted into and substantially dispersed through intercalation or exfoliation into the structure of the polymeric composition.

If desired, the various polymer compositions used to prepare the golf balls can additionally contain other additives such as plasticizers, pigments, antioxidants, U.V. absorbers, optical brighteners, or any other additives generally employed in plastics formulation or the preparation of golf balls.

Another particularly well-suited additive for use in the presently disclosed compositions includes compounds having the general formula:

$$(R_2N)_m—R'—(X(O)_nOR_y)_m,$$

where R is hydrogen, or a C_1-C_{20} aliphatic, cycloaliphatic or aromatic systems; R' is a bridging group comprising one or more C_1-C_{20} straight chain or branched aliphatic or alicyclic groups, or substituted straight chain or branched aliphatic or alicyclic groups, or aromatic group, or an oligomer of up to 12 repeating units including, but not limited to, polypeptides derived from an amino acid sequence of up to 12 amino acids; and X is C or S or P with the proviso that when X=C, n=1 and y=1 and when X=S, n=2 and y=1, and when X=P, n=2 and y=2. Also, m=1-3. These materials are more fully described in copending U.S. Provisional Patent Application No. 60/588,603, filed on Jul. 16, 2004, and U.S. patent application Ser. No. 11/182,170, filed Jul. 14, 2005, (now U.S. Pat. No. 7,767,759) the entire contents of which are herein incorporated by reference. These materials include caprolactam, oenantholactam, decanolactam, undecanolactam, dodecanolactam, caproic 6-amino acid, 11-aminoundecanoicacid, 12-aminododecanoic acid, diamine hexamethylene salts of adipic acid, azeleic acid, sebacic acid and 1,12-dodecanoic acid and the diamine nonamethylene salt of adipic acid, 2-aminocinnamic acid, L-aspartic acid, 5-aminosalicylic acid, aminobutyric acid; aminocaproic acid; aminocapyryic acid; 1-(aminocarbonyl)-1-cyclopropanecarboxylic acid; aminocephalosporanic acid; aminobenzoic acid; aminochlorobenzoic acid; 2-(3-amino-4-chlorobenzoyl)benzoic acid; aminonaphtoic acid; aminonicotinic acid; aminonorbornanecarboxylic acid; aminoorotic acid; aminopenicillanic acid; aminopentenoic acid; (aminophenyl)butyric acid; aminophenyl propionic acid; aminophthalic acid; aminofolic acid; aminopyrazine carboxylic acid; aminopyrazole carboxylic acid; aminosalicylic acid; aminoterephthalic acid; aminovaleric acid; ammonium hydrogencitrate; anthranillic acid; aminobenzophenone carboxylic acid; aminosuccinamic acid, epsilon-caprolactam; omega-caprolactam, (carbamoylphenoxy)acetic acid, sodium salt; carbobenzyloxy aspartic acid; carbobenzyl glutamine; carbobenzyloxyglycine; 2-aminoethyl hydrogensulfate; aminonaphthalenesulfonic acid; aminotoluene sulfonic acid; 4,4'-methylene-bis-(cyclohexylamine)carbamate and ammonium carbamate.

Most preferably the material is selected from the group consisting of 4,4'-methylene-bis-(cyclohexylamine)carbamate (commercially available from R.T. Vanderbilt Co., Norwalk, Conn. under the tradename Diak® 4), 11-aminoundecanoicacid, 12-aminododecanoic acid, epsilon-caprolactam; omega-caprolactam, and any and all combinations thereof.

In an especially preferred embodiment a nanofiller additive component in the golf ball is surface modified with a compatibilizing agent comprising the earlier described compounds having the general formula:

$$(R_2N)_m\text{—}R'\text{—}(X(O)_nOR_y)_m,$$

A most preferred embodiment would be a filler comprising a nanofiller clay material surface modified with an amino acid including 12-aminododecanoic acid. Such fillers are available from Nanonocor Co. under the tradename Nanomer 1.24TL.

Golf Ball Composition and Construction

Referring to the drawing in FIG. **1**, there is illustrated a golf ball **1**, which comprises a solid center or core **2**, which may be formed as a solid body and in the shape of the sphere.

In certain embodiments, the core of the balls may have a diameter of from 1.00 to 1.55, preferably from 1.1 to 1.50, and more preferably from 1.2 to 1.40, inches.

The core of the balls also may have a PGA compression of less than 80, preferably less than 70, more preferably less than 60, most preferably less than 50, and particularly less than 40. The PGA compression of the cores may range from 20 to 80, and preferably from 20 to 40.

In certain embodiments, the flexural modulus of the core material may be less than 20 kpsi, particularly less than about 15 kpsi, preferably less than 10 kpsi, and most preferably less than 8 kpsi.

The core and mantle layer materials may each exhibit a different material hardness. The difference between the core hardness and that of the next adjacent layer, as well as the difference in hardness between the various mantle layers may be greater than 5, preferably greater than 3, most preferably greater than or equal 2 units of Shore D.

Any combination of the above-described property ranges for the core may be employed, but illustrative specific embodiments of the core include a diameter of 1.00 to 1.55 inches, a PGA compression of less than 50, and a flexural modulus less than 15 kpsi; a diameter of 1.00 to 1.4 inches, a PGA compression of less than 50, and a flexural modulus less than 10 kpsi; and a diameter of 1.00 to 1.55 inches, a PGA compression of less than 40, and a flexural modulus less than 8 kpsi.

The core may be made from any of the polymers described above. In certain embodiments, the core is made from polybutadiene. In particular examples, the polybutadiene is the "major ingredient" of the core meaning that the polybutadiene constitutes at least 50, more particularly 60, most particularly 80, wt %, of all the ingredients in the core. In further embodiments, polybutadiene is the only polymer present in the core.

Mantle Layers

Again referring to the drawing in FIG. **1**, there are a series of mantle layers positioned over the core **2**. As shown in FIG. **1**, an inner mantle layer **3** is disposed outwardly adjacent of the core **2**, which is generally spherical. An intermediate mantle layer **4** is disposed outwardly of the inner mantle layer **3**. An outer mantle layer **5** is disposed outwardly of the intermediate mantle layer **4**.

Each of the mantle layers of the golf balls may have a thickness of less than 0.110 inch, more particularly less than 0.085 inch, and most particularly less than 0.075 inch.

As stated, one of the mantle layers has a higher flexural modulus than an outwardly disposed mantle layer. For example, in some embodiments, the inner mantle layer **3** has a higher flexural modulus than the intermediate mantle layer **4**. As another example, in some embodiments the intermediate mantle layer **4** has a higher flexural modulus than the outer mantle layer **5**.

In certain embodiments, the inner mantle may have a material Shore D hardness of 15 to 75, particularly 25 to 70, and more particularly 30 to 65. The inner mantle material may have a flexural modulus of 10 to 60, particularly 10 to 50, and more particularly 10 to 40, kpsi. The intermediate mantle material may have a flexural modulus of 5 to 90, particularly 10 to 70, and most particularly 20 to 60, kpsi, and a material Shore D hardness of 30 to 75, more particularly from 25 to 70, and most particularly from 40 to 65. The outer mantle material may have a material Shore D hardness of 35 to 80, particularly 40 to 75, and more particularly 45 to 70. The outer mantle material may have a flexural modulus of 10 to 90, particularly 15 to 80, and most particularly 20 to 70, kpsi.

The mantle layers may be made from any suitable material, particularly those materials described herein. In certain examples, the mantle layers may include a unimodal ionomer; a bimodal ionomer; a modified unimodal ionomer; a modified bimodal ionomer; a thermoset polyurethane; a polyester elastomer; a copolymer comprising at least one first co-monomer selected from butadiene, isoprene, ethylene or butylene and at least one second co-monomer selected from a (meth)acrylate or a vinyl arylene; a polyalkenamer; or any and all combinations or mixtures thereof. The above-listed mantle layer material(s) may be the "major ingredient" of the mantle layer meaning that the material(s) constitutes at least 50, more particularly 60, most particularly 80, wt %, of all the ingredients in the mantle layer. In further embodiments, the above-listed mantle layer material(s) is the only polymer(s) present in the mantle layer(s).

Cover Layer(s)

As shown in FIG. **1**, a cover layer **6** is disposed outwardly of the outer mantle layer **5**. The cover layer **6** may have a thickness of about 0.01 to about 0.10, preferably from about 0.02 to about 0.08, more preferably from about 0.025 to about 0.06 inch.

The cover layer of the balls may have a material hardness Shore D from about 30 to about 70, preferably from about 35 to about 65 or about 40 to about 62, more preferably from 47 to about 68 or about 45 to about 70, and most preferably from about 50 to about 65.

The cover layer may be made from any suitable material, particularly those disclosed herein. In preferred embodiments, illustrative examples include a thermoplastic elastomer, a thermoset polyurethane, a thermoplastic polyurethane, a thermoset polyurea, a thermoplastic polyurea, a unimodal ionomer, a bimodal ionomer, a modified unimodal ionomer, a modified bimodal ionomer; or any and all combinations or mixtures thereof. The above-listed cover layer material(s) may be the "major ingredient" of the cover layer meaning that the material(s) constitutes at least 50, more particularly 60, most particularly 80, wt %, of all the ingredients in the cover layer. In further embodiments, the above-listed cover layer material(s) is the only polymer(s) present in the cover layer(s).

A coating layer may be disposed on, or adjacent to, the cover layer. For example, the coating layer may be a thermoplastic resin based paint and/or a thermosetting resin based paint. Examples of such paints include vinyl acetate resin paints, vinyl acetate copolymer resin paints, EVA (ethylene-vinyl acetate copolymer resin) paints, acrylic ester (co)polymer resin paints, epoxy resin paints, thermosetting urethane resin paints, thermoplastic urethane resin paints, thermosetting acrylic resin paints, and unsaturated polyester resin paints. The coating layer may be transparent, semi-transparent or translucent.

The coefficient of restitution ("COR") of the golf balls may be greater than about 0.700, preferably greater than about 0.740, more preferably greater than 0.760, yet more preferably greater than 0.780, most preferably greater than 0.790, and especially greater than 0.795 at 125 ft/sec inbound velocity. In another embodiment, the COR of the golf balls may be greater than about 0.700, preferably greater than about 0.740, more preferably greater than 0.750, yet more preferably greater than 0.760, most preferably greater than 0.770, and especially greater than 0.780 at 143 ft/sec inbound velocity.

Method of Making the Golf Balls

The polymer(s), crosslinking agent(s), filler(s) and the like can be mixed together with or without melting them. Dry blending equipment, such as a tumble mixer, V-blender, ribbon blender, or two-roll mill, can be used to mix the compositions. The golf ball compositions can also be mixed using a mill, internal mixer such as a Banbury or Farrel continuous mixer, extruder or combinations of these, with or without application of thermal energy to produce melting. The various components can be mixed together with the cross-linking agents, or each additive can be added in an appropriate sequence to the milled unsaturated polymer. In another method of manufacture the cross-linking agents and other components can be added to the unsaturated polymer as part of a concentrate using dry blending, roll milling, or melt mixing.

The resulting mixture can be subjected to, for example, a compression or injection molding process, to obtain solid spheres for the core. The polymer mixture is subjected to a molding cycle in which heat and pressure are applied while the mixture is confined within a mold. The cavity shape depends on the portion of the golf ball being formed. The compression and heat liberates free radicals by decomposing one or more peroxides, which initiate cross-linking. The temperature and duration of the molding cycle are selected based upon the type of peroxide selected. The molding cycle may have a single step of molding the mixture at a single temperature for fixed time duration.

After core formation, the golf ball cover and any mantle layers are typically positioned over the core using one of three methods: casting, injection molding, a combination of injection molding and compression molding, or compression molding. Injection molding generally involves using a mold having one or more sets of two hemispherical mold sections that mate to form a spherical cavity during the molding process. The pairs of mold sections are configured to define a spherical cavity in their interior when mated. When used to mold an outer cover layer for a golf ball, the mold sections can be configured so that the inner surfaces that mate to form the spherical cavity include protrusions configured to form dimples on the outer surface of the molded cover layer. When used to mold a layer onto an existing structure, such as a ball core, the mold includes a number of support pins disposed throughout the mold sections. The support pins are configured to be retractable, moving into and out of the cavity perpendicular to the spherical cavity surface. The support pins maintain the position of the core while the molten material flows through the gates into the cavity between the core and the mold sections. The mold itself may be a cold mold or a heated mold

Compression molding of a ball cover or mantle layer typically requires the initial step of making half shells by injection molding the layer material into an injection mold. The half shells then are positioned in a compression mold around a ball core, whereupon heat and pressure are used to mold the half shells into a complete layer over the core, with or without a chemical reaction such as crosslinking. Compression molding also can be used as a curing step after injection molding. In such a process, an outer layer of thermally curable material is injection molded around a core in a cold mold. After the material solidifies, the ball is removed and placed into a mold, in which heat and pressure are applied to the ball to induce curing in the outer layer.

In certain specific embodiments, the core comprises polybutadiene;

the inner mantle layer and the intermediate mantle layer each individually comprise a unimodal ionomer; a bimodal ionomer; a modified unimodal ionomer; a modified bimodal ionomer; a thermoset polyurethane; a thermoset polyurea, a polyester elastomer; a copolymer comprising at least one first co-monomer selected from butadiene, isoprene, ethylene, propylene or butylene and at least one second co-monomer selected from a (meth)acrylate or a vinyl arylene; a polyalkenamer; or any and all combinations or mixtures thereof;

the outer mantle layer comprises a copolymer of ethylene and (meth)acrylic acid partially neutralized with a metal selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum or a combination thereof; or a blend of a polyamide and at least one maleic anhydride grafted polyolefin; and

the outer cover layer comprises a thermoset polyurethane; a thermoset polyurea; a polymer blend composition formed from a copolymer of ethylene and carboxylic acid as Component A, a hydroxyl-modified block copolymer of styrene and isoprene as Component B, and a metal cation as Component C; or a polymer blend composition formed from a copolymer of ethylene and carboxylic acid as Component A, a styrene-(ethylene-butylene)-styrene block copolymer as Component B, and a metal cation as Component C.

In other specific embodiments, the core comprises polybutadiene;

the inner mantle layer and the intermediate mantle layer each individually comprise a polyalkenamer;

the outer mantle layer comprises a copolymer of ethylene and (meth)acrylic acid partially neutralized with a metal selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum or a combination thereof; or a blend of a polyamide and at least one maleic anhydride grafted polyolefin; and

the outer cover layer comprises a thermoset polyurethane; or a thermoset polyurea.

In other specific embodiments, the core comprises polybutadiene;

the inner mantle layer and the intermediate mantle layer and the outer mantle layer each individually comprise a polyalkenamer; and

the outer cover layer comprises a thermoset polyurethane; or a thermoset polyurea.

In particular examples, the materials listed immediately above are the only polymers present in the core, inner mantle layer, intermediate mantle layer, outer mantle layer, and cover layer, respectively.

EXAMPLES

Example A

One example of a ball includes a core having a PGA compression of 35 and a flexural modulus of approximately 3.5 kpsi, an inner mantle having a flexural modulus of 30, an intermediate mantle having a flexural modulus of 18 kpsi, an outer mantle having a flexural modulus of 59 kpsi, and an outer cover layer having a flexural modulus of 11 kpsi. See also Table 1 below.

The golf ball of Example A follows the relationship of Equation 2, which is: FM(core)<FM(inner mantle)>FM(intermediate mantle)<FM(outer mantle)>FM(cover).

In other words, the flexural modulus generally increases from the core in a direction outward through the mantle layers, except that the inner mantle layer has a greater flexural modulus than the outwardly adjacent intermediate mantle layer.

Flexural modulus can be measured in accordance with ASTM D-790. This testing involves measuring the deflection of a specimen of the material supported at its ends and subjected to a known load. Thermoplastic specimens are made by using the injection molding process and a suitable cavity. Thermoset specimens are made by introducing a fully mixed material into a plaque mold designed to make parts to the appropriate thickness per ASTM D-790. The plaque is formed and cured using the compression molding process. The specimen's are cut or punched out of the plaque using a 1" wide by 4" long die supplied by Qualitest. The end result is a "flex bar" suitable for flex modulus testing.

Shore D hardness can be measured in accordance with ASTM D2240. Hardness of a layer can be measured on the ball, perpendicular to a land area between the dimples (referred to as "on-the-ball" hardness). The Shore D hardness of a material prior to fabrication into a ball layer can also be measured (referred to as "material" hardness) which is in accordance to ASTM D2240. Core or ball diameter may be determined using standard linear calipers or a standard size gauge.

Compression may be measured by applying a spring-loaded force to the sphere to be examined, with a manual instrument (an "Atti gauge") manufactured by the Atti Engineering Company of Union City, N.J. This machine, equipped with a Federal Dial Gauge, Model D81-C, employs a calibrated spring under a known load. The sphere to be tested is forced a distance of 0.2 inch (5 mm) against this spring. If the spring, in turn, compresses 0.2 inch, the compression is rated at 100; if the spring compresses 0.1 inch, the compression value is rated as 0. Thus more compressible, softer materials will have lower Atti gauge values than harder, less compressible materials. The value is taken shortly after applying the force and within at least 5 secs if possible. Compression measured with this instrument is also referred to as PGA compression.

The approximate relationship that exists between Atti or PGA compression and Riehle compression can be expressed as:

(Atti or PGA compression)=(160−Riehle Compression).

Thus, a Riehle compression of 100 would be the same as an Atti compression of 60.

The initial velocity of a golf ball after impact with a golf club is governed by the United States Golf Association ("USGA"). The USGA requires that a regulation golf ball can have an initial velocity of no more than 250 feet per second±2% or 255 feet per second. The USGA initial velocity limit is related to the ultimate distance that a ball may travel (280 yards±6%), and is also related to the coefficient of restitution ("COR"). The coefficient of restitution is the ratio of the relative velocity between two objects after direct impact to the relative velocity before impact. As a result, the COR can vary from 0 to 1, with 1 being equivalent to a completely elastic collision and 0 being equivalent to a completely inelastic collision. Since a ball's COR directly influences the ball's initial velocity after club collision and travel distance, golf ball manufacturers are interested in this characteristic for designing and testing golf balls.

Golf ball Sound Pressure Level, SPL, in decibels (dB) and Frequency in hertz (Hz) is measured to provide a quantitative measure of feel. In general, a ball with a lower frequency and SPL will feel softer. SPL is measured by dropping the ball from a height of 113 in onto a marble ("starnet crystal pink") stage of at least 12" square and 4.25 inches in thickness. The sound of the resulting impact is captured by a microphone positioned at a fixed proximity of 12 inches, and at an angle of 30 degrees from horizontal, from the impact position and resolved by software transformation into an intensity in db and a frequency in Hz.

Data collection is done as follows:

Microphone data is collected using a laptop PC with a sound card. An A-weighting filter is applied to the analog signal from the microphone. This signal is then digitally sampled at 44.1 KHz by the laptop data acquisition system for further processing and analysis. Data analysis is done as follows:

The data analysis is split into two processes:

a. Time series analysis that generates the root mean square (rms) sound pressure level (SPL) for each ball impact sound.

i. An rms SPL from a reference calibration signal is generated in the same manner as the ball data.

ii. The overall SPL (in decibels) is calculated from the reference signal for each ball impact sound.

iii. The median SPL is recorded based on 3 impact tests.

b. Spectral analyses for each ball impact sound

i. Fourier and Autoregressive spectral estimation techniques are employed to create power spectra.

ii. The frequencies (in cycles/sec—Hz) from highest level peaks representing the most active sound producing vibration modes of each ball are identified.

Impact durability may be tested with an endurance test machine. The endurance test machine is designed to impart repetitive deformation to a golf ball similar to a driver impact. The test machine consists of an arm and impact plate or club face that both rotate to a speed that generates ball speeds of approximately 155-160 mph. Ball speed is measured with two light sensors located 15.5" from impact location and are 11" apart. The ball is stopped by a net and if a test sample is not cracked will continue to cycle through the machine for additional impacts. For golf balls, if zero failures occur through in excess of 100 impacts per ball than minimal field failures will occur. For layers adjacent to the outer cover, fewer impacts are required since the cover typically "protects" the inner components of the golf ball. For the purpose of this study 75 impacts per component is considered sufficient.

Example B

Example B is similar to Example A, except the golf ball of Example B follows Equation 3, which is:

FM(core)<FM(inner mantle)<FM(intermediate mantle) >FM(outer mantle)>FM(cover). See also Table 2 below.

In other words, the flexural modulus generally increases from the core in a direction outward through the mantle layers, except that the intermediate mantle layer has a greater flexural modulus than the outwardly adjacent outer mantle layer.

Example C

Illustrative golf balls were made with the constructions shown in Tables 1 and 2.

TABLE 1

	Example Golf Ball According To Equation 2	5-Piece "Penta" Golf Ball	TP Red LDP	TP Black LDP
Preferred Specs				
Proto Name	PTP4-5	P4 Control	—	—
Core Size	1.260	1.260	1.420	1.480
Core Compression	35	35	50	70
FM (kpsi)	3.5	3.5	—	—
Inner Mantle Layer	NIM65	NIM55	—	—
Diameter(in)	1.380	1.380	—	—
FM (kpsi)	30	18	—	—
Intermediate Mantle Layer	NIM55	HPF-1000	HPF-1000	—
Diameter(in)	1.500	1.500	1.520	—
FM (kpsi)	18	30	30	—
Outer Mantle Layer	8150:9150	8150:9150	8150:9150	8150:9150
Diameter(in)	1.600	1.600	1.620	1.620
FM (kpsi)	59	59	59	59
Cover Blend	polyurethane	55D PU	55D PU	55D PU
FM (kpsi)	11	11	11	11
Robot Results				
175 mph Driver Spin(S10-065)	2630	2536	2667	2890
Launch Angle (deg.)	11.9	12.3	11.9	11.6
Ball speed (mph)	175.2	175.2	175.2	175.8
160 mph Driver Spin(S10-067)	2928	2895	2814	3072
Launch Angle (deg.)	11.9	11.7	11.7	11.5
Ball speed (mph)	160.8	161	160	161.1
5 Iron Spin(S10-069)	5633	5094	4803	5362
Launch Angle (deg.)	14.4	15.5	15.2	14.6
Ball speed (mph)	127	127.3	128	127.1
8 Iron Spin(S10-062)	7170	6913	6683	7446
Launch Angle (deg.)	20.6	21.1	21.1	20.1
Ball speed (mph)	109.4	109.9	109.5	109.4
100 yd PW Spin(S10-068)	10851	10476	10313	10583
Launch Angle (deg.)	25.8	26.2	26.1	25.8
Ball speed (mph)	95.3	95.7	95.1	95.4

TABLE 2

	Example Golf Ball According To Equation 3	5-Piece "Penta" Golf Ball
Preferred Specs		
Proto Name	PTP2-2	PTP2-C
Core Size	1.260	1.260
Core Compression	35	35
FM (kpsi)	3.5	3.5
Inner Mantle Layer	NIM55	NIM55
Diameter(in)	1.380	1.380
FM (kpsi)	18	18
Intermediate Mantle Layer	Surlyn 8150:9150	HPF-1000
Diameter(in)	1.500	1.500
FM (kpsi)	59	30
Outer Mantle Layer	HPF-1000	Surlyn 8150:9150
Diameter(in)	1.600	1.600
FM (kpsi)	30	59
Cover Blend	polyurethane	polyurethane
FM (kpsi)	11	11
Robot Results		
175 mph Driver Spin(S09-108)	3028	2678
Launch Angle (deg.)	11.9	12.4
Ball speed (mph)	175.3	175.9
160 mph Driver Spin(S09-119)	3022	2712
Launch Angle (deg.)	11.5	11.8
Ball speed (mph)	162.2	162.3
8 Iron Spin(S09-111)	7861	6932
Launch Angle (deg.)	19.9	20.9
Ball speed (mph)	110.9	111
30 yd PW Spin(S090-112)	7452	7104
Launch Angle (deg.)	31	31.7
Ball speed (mph)	42.6	42.8

NIM50 is a polyoctenamer compounded with 50 pph zinc diacrylate co-cross-linking agent. Likewise, NIM55 is a polyoctenamer compounded with 55 pph zinc diacrylate co-cross-linking agent, and NIM65 is a polyoctenamer compounded with 65 pph zinc diacrylate co-cross-linking agent.

SEPTON HG 252 is a styrenic copolymer available from Kuraray America Inc. HPF 1000 is a modified ionomer polymer available from DuPont. Surlyn 8150 and Surlyn 9150 are ionomers polymers available from DuPont.

As can be seen from Table 1, the material flexural modulus can be set to be higher for the inner mantle layer than intermediate mantle layer. According to one approach implemented in the PTP4-5 prototype according to Equation 2, NIM65 material having a material flexural modulus of about 30 kpsi can be selected for the inner mantle layer, and NIM55 material having a flexural modulus of about 18 kpsi can be selected for the intermediate mantle layer. In contrast to the 5-piece "Penta" golf ball which has increasing flexural modulus from core to the outer mantle layer, the PTP4-5 prototype according to Equation 2 has higher 5 iron, 8 iron, and 100 yd PW backspin while maintaining low driver spin for long distance. Typical tour players generate high iron backspin due to higher than average clubhead speeds and their ability to trap or pinch the ball between the ground and club face. A golf ball that spins too much on these types of shots will typically have a "ballooning" type trajectory and will be more affected by wind. The 5-piece "Penta" golf ball is ideal for these types of players since it helps reduce spin on the iron shots for lower more consistent flight into the wind. The PTP4-5 prototype offers low driver spin, similar to the 5-piece "Penta" ball, but has more spin on the iron shots, which is ideal for a player needing more hold on shots into the green. In Table 1, the TP Black has spin characteristics most similar to the PTP4-5 prototype. However, in FIG. **2** the TP Black has a higher Frequency and SPL than PTP4-5, which is an indication that the ball will feel firmer when struck with a club. By contrast, the PTP4-5 prototypes offers increased iron spin and soft feel.

Table 2 is similar to Table 1, except Table 2 shows test results of an Equation 3 prototype golf ball compared to the 5-piece Penta golf ball. According to Equation 3, FM (intermediate mantle layer)>FM (outer mantle layer). According to one approach implemented in the PTP2-2 prototype according to Equation 3, Surlyn 8150:9150 material having a material flexural modulus of about 59 kpsi can be selected for the intermediate mantle layer, and HPF1000 material having a flexural modulus of about 30 kpsi can be selected for the outer mantle layer. In contrast to the 5-piece "Penta" golf ball which has increasing flexural modulus, the PTP2-2 prototype has significantly higher 8 iron spin and slightly higher 30 yd wedge spin.

FIG. **2** is a graph of frequency vs. sound level SPL for exemplary golf balls according to this application also showing exemplary conventional golf balls for comparison. The conventional TP Black LDP golf ball produces higher sound levels at higher frequencies than the prototype PTP2 4-5 ball, which is a ball constructed according to this application. The sound of the PTP2 4-5 ball, at about 89.5 dB and 3400 Hz according to FIG. **2**, is about the same as the Titleist Pro V1, TP Red LDP, and P4 Control(5-piece "Penta"). These results are an indication that the PTP2 4-5 offers similar feel to these other soft balls and significantly softer than TP Black LDP

All the cores were made from a blend of polybutadiene, zinc oxide, barium sulfate, zinc diacrylate, peroxide and 2,3,5,6-tetrachloro-4-pyridinethiol (TCPT). The cores were made by the standard process that includes mixing the core material in a two roll mill, extruding the mixture, and then forming and curing the cores under heat and pressure in a compression molding cycle. The inner layers were all made by injection molding. The NIM65 and NIM55 materials use the injection molding process to form the material around the inner sphere than require a compression molding cycle to cure or cross-link the material. However, any type of cover layer could have been applied to the balls. In the examples, the hardness measurements are on the ball/mantle.

The results shown in Tables 1-2 demonstrate that a ball with a presently disclosed 5-piece construction exhibits higher iron backspin while maintaining soft feel.

In view of the many possible embodiments to which the principles of this disclosure may be applied, it should be recognized that the illustrated embodiments are only preferred examples and should not be taken as limiting in scope. Rather, the scope of protection is defined by the following claims. We therefore claim all that comes within the scope and spirit of these claims.

We claim:

1. A golf ball comprising:

(a) a core material having a material flexural modulus of less than 20 kpsi;

(b) an inner mantle layer material;

(c) an intermediate mantle layer material;

(d) an outer mantle layer material; and

(e) at least one cover layer material;

wherein the material of each of (a), (b), (c) and (d) has a material flexural modulus and the material flexural modulus increases from the core material (a) to the mantle layers (b), (c) and (d), and wherein within the mantle layers, there is at least one mantle layer that has a material flexural modulus greater than the material flexural modulus of an outwardly adjacent mantle layer.

2. The golf ball of claim **1**, wherein the core has a PGA compression of less than 50.

3. The golf ball of claim **1**, wherein the inner mantle layer has a material flexural modulus of 10 to 60 kpsi.

4. The golf ball of claim **3**, wherein the intermediate mantle layer has a material flexural modulus of 10 to 90 kpsi.

5. The golf ball of claim **4**, wherein the outer mantle layer has a material flexural modulus of 10 to 90 kpsi.

6. The golf ball of claim **1**, wherein the core material has a flexural modulus of less than 15 kpsi and a PGA compression of less than 50.

7. The golf ball of claim **1**, wherein the inner mantle layer, the intermediate mantle layer, and the outer mantle layer each individually comprises a unimodal ionomer; a bimodal ionomer; a modified unimodal ionomer; a modified bimodal ionomer; a thermoset polyurethane; a polyester elastomer; a copolymer comprising at least one first co-monomer selected from butadiene, isoprene, ethylene or butylene and at least one second co-monomer selected from a (meth)acrylate or a vinyl arylene; a polyalkenamer; or any and all combinations or mixtures thereof.

8. The golf ball of claim **1**, wherein the cover layer comprises a polyurethane, a polyurea, or a combination or mixture thereof.

9. The golf ball of claim **1**, wherein the outer mantle layer has a flexural modulus of at least 25 kpsi.

10. The golf ball of claim **1**, wherein the core has a PGA compression of less than 60.

11. The golf ball of claim **1**, wherein a core/inner mantle layer/intermediate mantle layer combined construct has a PGA compression of at least 40.

12. The golf ball of claim **1**, wherein a core/inner mantle layer/intermediate mantle layer combined construct has a PGA compression of at least 50.

13. The golf ball of claim **1**, wherein a core/inner mantle layer/intermediate mantle layer combined construct has a PGA compression of 30 to 70.

14. The golf ball of claim **1**, wherein the flexural modulus of the inner mantle layer is greater than the flexural modulus of the intermediate mantle layer.

15. The golf ball of claim **14**, wherein the flexural modulus of the outer mantle layer is greater than the flexural modulus of the inner mantle layer.

16. The golf ball of claim **1**, wherein the flexural modulus of the intermediate mantle layer is greater than the flexural modulus of the outer mantle layer.

17. The golf ball of claim **16**, wherein the flexural modulus of the outer mantle layer is greater than the flexural modulus of the inner mantle layer.

18. The golf ball of claim **1**, wherein the inner mantle layer material comprises a polyoctenamer, the intermediate mantle layer material comprises a modified ionomer, the outer mantle layer material comprises at least one high acid ionomer having a (meth)acrylic content of from about 16 weight % to about 35 weight % and the cover layer material comprises a thermoset polyurethane or thermoset polyurea.

19. The golf ball of claim **1**, wherein the inner mantle layer material comprises a polyoctenamer, the intermediate mantle layer material comprises a a polyoctenamer, the outer mantle layer material comprises at least one high acid ionomer having a (meth)acrylic content of from about 16 weight % to about 35 weight % and the cover layer material comprises a thermoset polyurethane or thermoset polyurea.

20. The golf ball of claim **1**, wherein the inner mantle layer material comprises a polyoctenamer, the intermediate mantle layer material comprises a polyoctenamer, the outer mantle layer material comprises a polyoctenamer, and the cover layer material comprises a thermoset polyurethane or thermoset polyurea.

21. A five-piece golf ball comprising:
(a) a core material having a flexural modulus of less than 15 kpsi;
(b) an inner mantle layer material adjacent to the core material, wherein the inner mantle layer material has a flexural modulus of 10-60 kpsi;
(c) an intermediate mantle layer material adjacent to the inner mantle layer material, wherein the intermediate mantle layer material has a flexural modulus of 10-40 kpsi;
(d) an outer mantle layer material adjacent to the intermediate mantle layer material, wherein the outer mantle layer material has a flexural modulus of 30-90 kpsi; and
(e) an outer cover layer material; and
wherein the inner mantle layer (b) has a greater flexural modulus than the intermediate mantle layer (c).

22. The golf ball of claim 21, wherein the core material has a flexural modulus of less than 10 kpsi, the inner mantle layer material has a flexural modulus of 15-50 kpsi, the intermediate mantle layer material has a flexural modulus of 12-35 kpsi, and the outer mantle layer has a flexural modulus of 40-75 kpsi; and wherein the inner mantle layer has a greater flexural modulus than the intermediate mantle layer.

23. The golf ball of claim 21, wherein the core material has a PGA compression of less than 50.

24. The golf ball of claim 21, wherein the inner mantle layer, the intermediate mantle layer, and the outer mantle layer each individually comprises a unimodal ionomer; a bimodal ionomer; a modified unimodal ionomer; a modified bimodal ionomer; a thermoset polyurethane; a polyester elastomer; a copolymer comprising at least one first co-monomer selected from butadiene, isoprene, ethylene or butylene and at least one second co-monomer selected from a (meth)acrylate or a vinyl arylene; a polyalkenamer; or any and all combinations or mixtures thereof.

25. The golf ball of claim 24, wherein the cover layer comprises a polyurethane, a polyurea, or a combination or mixture thereof.

26. The golf ball of claim 21, wherein the outer mantle layer has a material flexural modulus of at least 30 kpsi.

27. The golf ball of claim 21, wherein the inner mantle layer material comprises a polyoctenamer, the intermediate mantle layer material comprises a modified ionomer, the outer mantle layer material comprises at least one high acid ionomer having a (meth)acrylic content of from about 16 weight % to about 35 weight % and the cover layer material comprises a thermoset polyurethane or thermoset polyurea.

28. The golf ball of claim 21, wherein the inner mantle layer material comprises a polyoctenamer, the intermediate mantle layer material comprises a a polyoctenamer, the outer mantle layer material comprises at least one high acid ionomer having a (meth)acrylic content of from about 16 weight % to about 35 weight % and the cover layer material comprises a thermoset polyurethane or thermoset polyurea.

29. The golf ball of claim 21, wherein the inner mantle layer material comprises a polyoctenamer, the intermediate mantle layer material comprises a polyoctenamer, the outer mantle layer material comprises a polyoctenamer, and the cover layer material comprises a thermoset polyurethane or thermoset polyurea.

30. A five-piece golf ball comprising:
(a) a core material having a flexural modulus of less than 15 kpsi;
(b) an inner mantle layer material adjacent to the core material, wherein the inner mantle layer material has a flexural modulus of 2-35 kpsi;
(c) an intermediate mantle layer material adjacent to the inner mantle layer material, wherein the intermediate mantle layer material has a flexural modulus of 30-90 kpsi;
(d) an outer mantle layer material adjacent to the intermediate mantle layer material, wherein the outer mantle layer material has a flexural modulus of 20-60 kpsi; and
(e) an outer cover layer material; and
wherein the intermediate mantle layer (c) has a greater flexural modulus than the outer mantle layer (d).

31. The golf ball of claim 30, wherein the core material has a flexural modulus of less than 10 kpsi, the inner mantle layer material has a flexural modulus of 12-35 kpsi, the intermediate mantle layer material has a flexural modulus of 40-75 kpsi, and the outer mantle layer has a flexural modulus of 25-50 kpsi; and wherein the intermediate mantle layer has a greater flexural modulus than the outer mantle layer.

32. The golf ball of claim 30, wherein the core material has a PGA compression of less than 50.

33. The golf ball of claim 30, wherein the inner mantle layer, the intermediate mantle layer, and the outer mantle layer each individually comprises a unimodal ionomer; a bimodal ionomer; a modified unimodal ionomer; a modified bimodal ionomer; a thermoset polyurethane; a polyester elastomer; a copolymer comprising at least one first co-monomer selected from butadiene, isoprene, ethylene or butylene and at least one second co-monomer selected from a (meth)acrylate or a vinyl arylene; a polyalkenamer; or any and all combinations or mixtures thereof.

34. The golf ball of claim 33, wherein the cover layer comprises a polyurethane, a polyurea, or a combination or mixture thereof.

35. The golf ball of claim 30, wherein the outer mantle layer has a material flexural modulus of at least 20 kpsi.

36. The golf ball of claim 30, wherein the inner mantle layer material comprises a polyoctenamer, the intermediate mantle layer material comprises a modified ionomer, the outer mantle layer material comprises at least one high acid ionomer having a (meth)acrylic content of from about 16 weight % to about 35 weight % and the cover layer material comprises a thermoset polyurethane or thermoset polyurea.

37. The golf ball of claim 30, wherein the inner mantle layer material comprises a polyoctenamer, the intermediate mantle layer material comprises a a polyoctenamer, the outer mantle layer material comprises at least one high acid ionomer having a (meth)acrylic content of from about 16 weight % to about 35 weight % and the cover layer material comprises a thermoset polyurethane or thermoset polyurea.

38. The golf ball of claim 30, wherein the inner mantle layer material comprises a polyoctenamer, the intermediate mantle layer material comprises a polyoctenamer, the outer mantle layer material comprises a polyoctenamer, and the cover layer material comprises a thermoset polyurethane or thermoset polyurea.

39. A golf ball comprising:
(a) a core having a PGA compression of less than 50;
(b) an inner mantle layer;
(c) an intermediate mantle layer over the inner mantle layer;
(d) an outer mantle layer over the intermediate mantle layer; and
(e) an outer cover layer;
wherein the outer cover layer has a lower flexural modulus than the intermediate mantle layer or the intermediate mantle layer has a lower flexural modulus than the inner mantle layer;

wherein the golf ball has sufficient impact durability and a golf ball frequency of less than 4000 Hz.

40. The golf ball of claim **39**, wherein the inner mantle layer material comprises a polyoctenamer, the intermediate mantle layer material comprises a modified ionomer, the outer mantle layer material comprises at least one high acid ionomer having a (meth)acrylic content of from about 16 weight % to about 35 weight % and the cover layer material comprises a thermoset polyurethane or thermoset polyurea.

41. The golf ball of claim **39**, wherein the inner mantle layer material comprises a polyoctenamer, the intermediate mantle layer material comprises a a polyoctenamer, the outer mantle layer material comprises at least one high acid ionomer having a (meth)acrylic content of from about 16 weight % to about 35 weight % and the cover layer material comprises a thermoset polyurethane or thermoset polyurea.

42. The golf ball of claim **39**, wherein the inner mantle layer material comprises a polyoctenamer, the intermediate mantle layer material comprises a polyoctenamer, the outer mantle layer material comprises a polyoctenamer, and the cover layer material comprises a thermoset polyurethane or thermoset polyurea.

43. The golf ball of claim **1**, wherein:

the core comprises polybutadiene;

the inner mantle layer and the intermediate mantle layer each individually comprise a unimodal ionomer; a bimodal ionomer; a modified unimodal ionomer; a modified bimodal ionomer; a thermoset polyurethane; a polyester elastomer; a copolymer comprising at least one first co-monomer selected from butadiene, isoprene, ethylene, propylene or butylene and at least one second co-monomer selected from a (meth)acrylate or a vinyl arylene; a polyalkenamer; or any and all combinations or mixtures thereof;

the outer mantle layer comprises a copolymer of ethylene and (meth)acrylic acid partially neutralized with a metal selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum or a combination thereof; or a blend of a polyamide and at least one maleic anhydride grafted polyolefin; and

the outer cover layer comprises a thermoset polyurethane; a thermoset polyurea; a polymer blend composition formed from a copolymer of ethylene and carboxylic acid as Component A, a hydroxyl-modified block copolymer of styrene and isoprene as Component B, and a metal cation as Component C; or a polymer blend composition formed from a copolymer of ethylene and carboxylic acid as Component A, a styrene-(ethylene-butylene)-styrene block copolymer as Component B, and a metal cation as Component C.

44. The golf ball of claim **43**, wherein the polybutadiene of the core is obtained via a lanthanum rare earth catalyst.

45. The golf ball of claim **44**, wherein the polybutadiene of the core further comprises a pyridine peptizer that also includes a chlorine functional group and a thiol functional group.

46. The golf ball of claim **45**, wherein the inner mantle layer and the intermediate mantle layer each individually comprise polyoctenamer; a hydroxyl-modified block copolymer of styrene and isoprene; a high acid content modified ionomers; or a mixture thereof.

47. The golf ball of claim **21**, wherein:

the core comprises polybutadiene;

the inner mantle layer and the intermediate mantle layer each individually comprise a unimodal ionomer; a bimodal ionomer; a modified unimodal ionomer; a modified bimodal ionomer; a thermoset polyurethane; a polyester elastomer; a copolymer comprising at least one first co-monomer selected from butadiene, isoprene, ethylene, propylene or butylene and at least one second co-monomer selected from a (meth)acrylate or a vinyl arylene; a polyalkenamer; or any and all combinations or mixtures thereof;

the outer mantle layer comprises a copolymer of ethylene and (meth)acrylic acid partially neutralized with a metal selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum or a combination thereof; or a blend of a polyamide and at least one maleic anhydride grafted polyolefin; and

the outer cover layer comprises a thermoset polyurethane; a thermoset polyurea; a polymer blend composition formed from a copolymer of ethylene and carboxylic acid as Component A, a hydroxyl-modified block copolymer of styrene and isoprene as Component B, and a metal cation as Component C; or a polymer blend composition formed from a copolymer of ethylene and carboxylic acid as Component A, a styrene-(ethylene-butylene)-styrene block copolymer as Component B, and a metal cation as Component C.

48. The golf ball of claim **30**, wherein:

the core comprises polybutadiene;

the inner mantle layer and the intermediate mantle layer each individually comprise a unimodal ionomer; a bimodal ionomer; a modified unimodal ionomer; a modified bimodal ionomer; a thermoset polyurethane; a polyester elastomer; a copolymer comprising at least one first co-monomer selected from butadiene, isoprene, ethylene, propylene or butylene and at least one second co-monomer selected from a (meth)acrylate or a vinyl arylene; a polyalkenamer; or any and all combinations or mixtures thereof;

the outer mantle layer comprises a copolymer of ethylene and (meth)acrylic acid partially neutralized with a metal selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, lead, tin, zinc, aluminum or a combination thereof; or a blend of a polyamide and at least one maleic anhydride grafted polyolefin; and

the outer cover layer comprises a thermoset polyurethane; a thermoset polyurea; a polymer blend composition formed from a copolymer of ethylene and carboxylic acid as Component A, a hydroxyl-modified block copolymer of styrene and isoprene as Component B, and a metal cation as Component C; or a polymer blend composition formed from a copolymer of ethylene and carboxylic acid as Component A, a styrene-(ethylene-butylene)-styrene block copolymer as Component B, and a metal cation as Component C.

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